

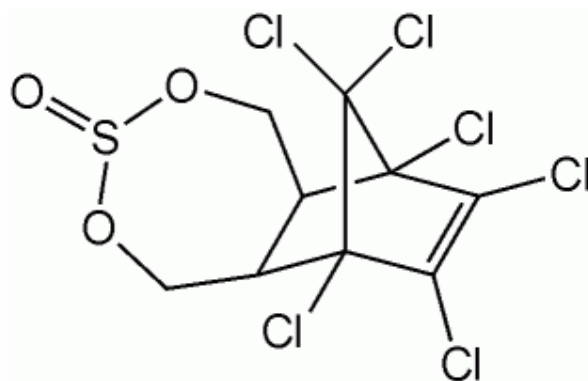
**DRAFT**

**ENDOSULFAN**

**RISK CHARACTERIZATION DOCUMENT**

**Volume III**

**Environmental Fate**



(Major changes are underlined: pp. 10; 20-21; 40)

**Environmental Monitoring Branch  
Department of Pesticide Regulation  
California Environmental Protection Agency**

**November 2007**

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**RISK CHARACTERIZATION DOCUMENT**

**Volume III**

**Environmental Fate**

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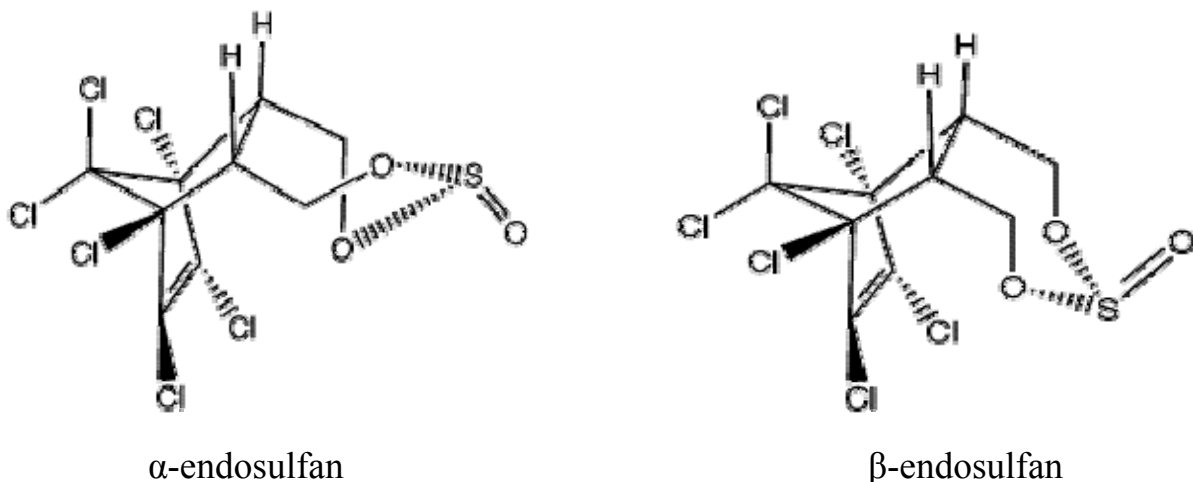
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### Chemical structure characteristics and physicochemical properties

Endosulfan is a chlorinated hydrocarbon insecticide and acaricide in the class of chlorinated cyclodiene, a member of organochlorine family (Table 1). Its distinguishing feature is that it contains only one double bond, whereas the most of the cyclodiene class members contain two double bonds. The molecular structures of its two stereochemical isomers,  $\alpha$ - and  $\beta$ -endosulfan are depicted in Figure 1. The  $\alpha$ -isomer is asymmetric and exists as two twist chair forms. The  $\beta$ -isomer is symmetric. Isomerization was found to be favored from  $\beta$ - to  $\alpha$ -endosulfan (Schmidt, et al., 2001; Walse, et al., 2003).

**Table 1. Endosulfan identity**

Common Name:	Endosulfan	
Chemical Name:		
IUPAC	6, 7, 8, 9, 10, 10-hexachloro-1, 5, 5a, 6, 9, 9a-hexahydro-6, 9-methano-2, 4, 3-benzodioxathiepin 3-oxide	
Chemical Abstract	6, 9-methano-2, 4, 3-benzodioxathiepin-6, 7, 8, 9, 10, 10-hexachloro1, 5, 5, 6, 9, 9-hexahydro-3-oxide	
Chemical Family	Organochlorine	
Trade Name:	Thiodan®, Thionex®	
CAS Registry Number:	959-98-8	$\alpha$ -Endosulfan
	33213-65-9	$\beta$ -Endosulfan
	115-29-7	Technical Endosulfan (a mixture of $\alpha$ - & $\beta$ -isomer)
	1031-07-8	Endosulfan sulfate
Molecular Formula:	C <sub>9</sub> H <sub>6</sub> Cl <sub>6</sub> O <sub>3</sub> S	
Molecular Weight:	406.96	

**Figure 1. Chemical structures of endosulfan (source from PANNA, 2007)**

Technical grade endosulfan is a diastereomeric mixture of roughly 70%  $\alpha$ -isomer and 30%  $\beta$ -isomer (US EPA, 2002), along with impurities and degradation products. Pure endosulfan is a colorless crystal; but technical grade is brown in color, ranging from light to dark depending on impurities. Its odor is similar to hexachlorocyclopentadiene, sometimes mixed with sulfur dioxide. Selected physiochemical properties for the major endosulfan forms in the environment are listed in Table 2.

**Table 2. Physicochemical properties of endosulfan\***

	$\alpha$ - isomer	$\beta$ - isomer	Technical grade endosulfan	Endosulfan sulfate
Melting point (°C)	108-110	208-210	70-124	181-201 <sup>b</sup>
Solubility (mg/L @25 °C)	0.33 <sup>b</sup>	0.32 <sup>b</sup>	0.33 <sup>a</sup>	0.22 <sup>b</sup>
Vapor pressure (mm Hg, @25 °C)	$3.0 \times 10^{-6}$	$7.2 \times 10^{-7}$	$1.0 \times 10^{-5}$	$8.3 \times 10^{-9b}$
Bulk density (g/ml)			1.8 <sup>c</sup>	
Flammability			Not flammable <sup>b</sup>	
Henry's Law constant	$4.9 \times 10^{-6d}$	$1.2 \times 10^{-6d}$	$1.6 \times 10^{-5d}$	
(atm m <sup>3</sup> mol <sup>-1</sup> @ 25 °C)	$1.3 \times 10^{-4b}$	$2.1 \times 10^{-5b}$		
Log K <sub>ow</sub> (pH 5.1)	4.6-4.7 <sup>b</sup>	4.3-4.8 <sup>b</sup>	4.5-5.7	
Koc (cm <sup>3</sup> /g)	10600	13600	12,000 <sup>a</sup>	
Soil aerobic half-life (days)	19-33 <sup>b</sup>	42-58 <sup>b</sup>	31.6 <sup>a</sup>	100-150 <sup>b</sup>
Soil anaerobic half-life (days)			148 <sup>a</sup>	
Hydrolysis half-life (days)	11 (pH 7)	19 (pH 7)	14.8 <sup>a</sup>	
Photolysis half-life (days)			>200 <sup>b</sup>	

\* Data in this table are from US EPA, 2002 except for denoted ones.

<sup>a</sup>DPR chemical database (DPR, 2004).

<sup>b</sup>GFEA, 2004.

<sup>c</sup>Footprint, 2007.

<sup>d</sup>Calculated from vapor pressure and solubility.

Endosulfan is a broad-spectrum non-systemic insecticide and acaricide with contact and stomach action. It is used to control sucking, chewing, and boring insects on a wide variety of vegetables, fruits, grains, cotton, and tea, as well as ornamental shrubs, vines, and trees (Tomlin, 1994).

Formulations of endosulfan include emulsifiable concentrate, wettable powder, ultra-low volume (ULV) liquid, and smoke tablets. Endosulfan is compatible with many other pesticides and may be found in formulations with dimethoate, malathion, methomyl, monocrotophos, pirimicarb, triazophos, fenoprop, parathion, petroleum oils, and oxine-copper. It is not compatible with alkaline materials because it is vulnerable to hydrolysis (US EPA, 2002). Application of endosulfan can be made using groundboom sprayer, fixed-wing aircraft, chemigation, airblast sprayer, rights-of-way sprayer, low pressure handwand sprayer, high pressure handwand sprayer, backpack sprayer and dip treatment (US EPA, 2002).

## **Regulation**

Endosulfan is classified in the U.S. Environmental Protection Agency (US EPA) toxicity category I (40 CFR 156.60-156.62). Pesticide labels for products containing endosulfan must bear the Signal Words “DANGER – POISON” or “DANGER” depending on formulation.

US EPA has established a series of regulations for endosulfan applications since it was registered as a pesticide in the U.S. in 1954 to control agricultural insect and mite pests. In 1981 and 1982, a Registration Standard and a Guidance Document were issued for endosulfan requiring additional generic and product-specific data for the manufacturing products of the technical registrants (US EPA 2002). In 1988, Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) was amended to accelerate the reregistration of products with active ingredients registered prior to November 1, 1984 to ensure that they meet more stringent standards, and to report product information concerning unreasonable adverse effects to US EPA. In 1990, the Update Endosulfan Reregistration Standard was issued, which summarized regulatory conclusions based on available residue chemistry data and specified the additional data required for reregistration purposes. Between 1985 and 1994, eight data call-ins concerned potential formation of chlorinated dibenzo-p-dioxins and dibenzofurans and residue chemistry data deficiencies. In 1996, the Food Quality Protection Act (FQPA) amended and strengthened the standard for establishing tolerances under the Federal Food, Drug, and Cosmetic Act (FFDCA). To implement provisions of the FQPA of 1996, US EPA considered the special sensitivity of infants and children to pesticides, as well as aggregate exposure of the public to pesticide residues from all sources, and the cumulative effects of pesticides and other compounds with common mechanisms of toxicity. In November 2002, the reregistration eligibility decision (RED) concluded that agricultural uses of endosulfan based on approved labeling pose occupational risks of concern and ecological risks that constitute unreasonable adverse effects on the environment. However, these risks can likely be mitigated to levels below concern through changes to pesticide labeling and formulations. US EPA has determined that endosulfan is eligible for reregistration with conditions (1) additional required data will confirm this decision for occupational exposures associated with the application of dip treatment to roots or whole plants and ecological risks; and (2) the risk mitigation outlined in the RED are adopted, and label amendments are made to reflect these measures. If vulnerable areas in specific geographic areas

are identified as a result of the stakeholder process, additional ecological risk mitigation measures may be necessary to protect especially sensitive organisms (US EPA, 2002). In September 2006, US EPA revoked certain tolerances and is modifying and establishing new tolerances for endosulfan and other pesticides (US EPA, 2006a).

In 1991 the federal technical registrants amended labels to incorporate a 300-foot spray drift buffer for aerial applications between treated areas and water bodies. This setback was adopted to address concerns about contamination of water and risks to aquatic organisms. In 2000, technical product labels were amended to remove all residential use patterns. The registrants have further restricted the annual maximum use rate to 3 pounds active ingredient per acre for all uses.

In addition to the federal regulations, California amended its more stringent policies and regulation for endosulfan uses. Pursuant to Section 14004.5 of the Title 3, Food and Agricultural Code (FAC), endosulfan is designated a restricted use material in section 6400 (e) of the FAC with exceptions only for home, structural, industrial, institutional, or public agency vector control districts uses that are pursuant to section 2426 of the Health and Safety Code. Restricted materials are possessed and used by persons only under permit of the county agricultural commissioner.

Pursuant to Section 13127 of the FAC, the Birth Defect Prevention Act (Statutes 1984, Chapter 669) mandates the listing of endosulfan in section 6198.5 of FAC. The 200 priority pesticide active ingredients listed in this section have the most significant data gaps and widespread use and are suspected to be hazardous to people. Currently, all data requirements for endosulfan have been submitted to the Department of Pesticide Regulation (DPR. 2007a).

Pursuant to Section 13143 of the FAC, Pesticide Pollution Prevention Act (AB 2021) mandates data call-in of chemistry and environmental fate studies for products with active ingredient of endosulfan including degradation products in specific studies. Currently, all data requirements for endosulfan have been submitted to the Department of Pesticide Regulation (DPR. 2007a)

### **Use Profile in California**

Endosulfan has been widely used in California. Currently, there are six products containing endosulfan as an active ingredient (a.i.) registered in California. Two emulsifiable concentrate insecticides (34% a.i.) and three wettable powder formulations (50% a.i.) are registered for agricultural or commercial use only. The other one is a technical insecticide (95% a.i.) for manufacture of insecticides and acaricides only. The registered endosulfan products are used to control aphids, thrips, beetles, foliar feeding larvae, leafminer, mites, borers, cutworms, fruitworms, bugs, whiteflies, leafhoppers, loopers, and weevils for a wide variety of fruit trees, vegetables, and other crops, such as apples, nectarines, peaches, prune, lettuce, tomatoes, cantaloupe, grapes, melons, vegetable peppers, broccoli, sugarbeet, cauliflower, carrots, cabbage, rape, squash, cucumber, strawberry, alfalfa, corn, potato, beans, cotton, walnut, pecan, etc. The application rates vary depending on target crop, product used, and pest to be controlled. Labeled application rates are summarized in Table 3.



**Table 3. Summary of pesticide application label rates for major product uses in California**

Crops	Pests to be Controlled	Application Rates	
		WP or WSB*	EC**
Apples, nectarines, peaches, prunes, and citrus	Aphids, mite, leafhopper, stink bugs, and borers	1 lb/100 gals or max. 8 lbs/acre	0.66qt/100 gals or max. 3.33 qts/acre
Lettuce, broccoli, cabbage, cauliflower, cucumbers, melons, squash, peppers, carrots, potatoes, sweet potatoes, strawberries, tomatoes, sugarbeets, and beans	Aphids, loopers, worms, whiteflies, moth larvae, beetles, leafhoppers, spittlebugs, stink bugs, and borers	1-2 lbs/acre	0.66-1.33 qts/acre
Alfalfa (for seed only)	Spotted alfalfa aphid		2.66 pints/acre
Strawberries	Cyclamen mite,	4 lbs/acre in 400 gals water	2.66 qts/ acre in 400 gals water or 1.33-2 qts/ acre
Sweet corn (vegetable)	Aphids, whiteflies Earworms		1.33 qts/acre 2 qts/acre
Grapes	Leafhoppers, chafers	1 lb/100 gals or 2-3 lbs/acre	0.66 qt/100 gals or 1.5-2 qts/acre
Walnut	Aphids	3-4 lbs/acre	
Pecans	Spittlebug, aphid, and nut casebearer	1.5 lb/100 gals max. 8 lbs/acre	1 qt/100 gals
Cotton	Leaf perforator	2 lbs/acre	1.33-2 qts/acre
	Aphids		0.5-1 qt/acre
	Worms, loopers, leafhoppers, lygus bugs, stink bugs, and thrips		1.33-2 qts/acre 2 qts/acre
	Whiteflies		1.5 qts/acre

\*Wettable Powder or Water Soluble Bags

\*\*Emulsifiable Concentrate

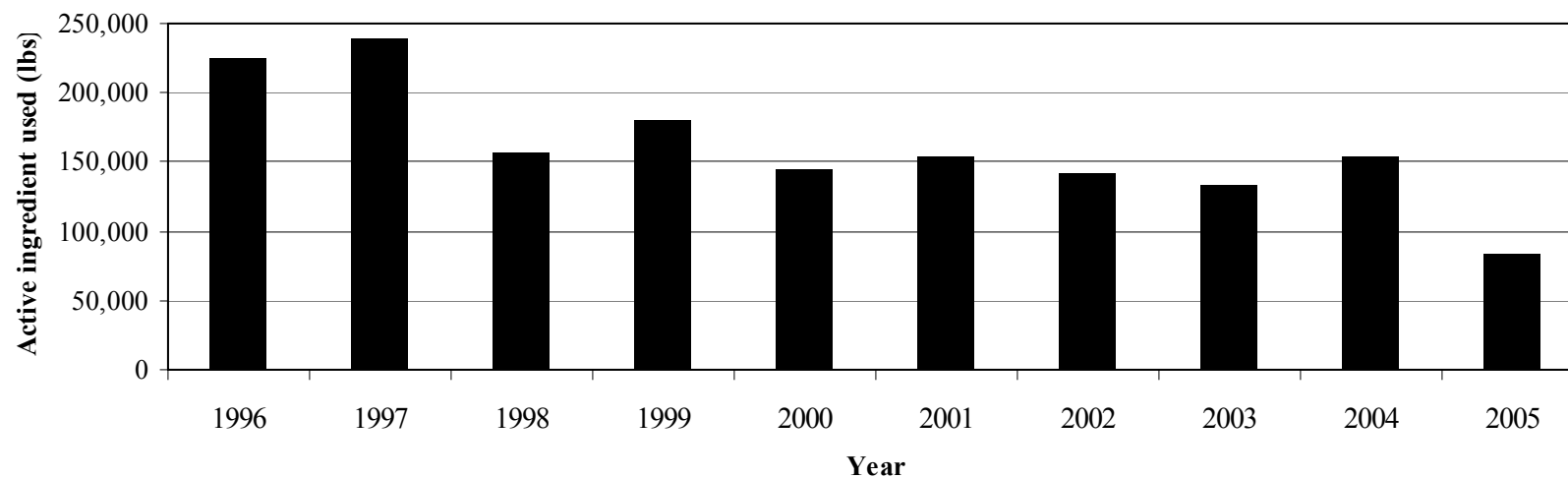
DPR fully implemented agricultural pesticide use reporting system in 1990. All agricultural use must be reported monthly to the county agricultural commissioners. The county agricultural commissioners forward these data to DPR. DPR annually compiles the data and makes pesticide use reports available to the public. Agricultural use also includes applications to parks, golf courses, cemeteries, rangeland, pastures, and rights-of-way. Although use in structural pest control is excluded, the use of pesticides designated as restricted materials pursuant to section 14004.5 of the Food and Agricultural Code must be reported as non-agricultural use. For non-agricultural applications, detailed geographic information such as base meridian/township/range/section is not provided. In this document, pesticide use data were queried from DPR's database (DPR, 2007b) with exclusion of outliers (Wilhoit, 1998).

In recent ten years, annual endosulfan use reported decreased from 238,635 pounds in 1997 to 83,242 pounds of active ingredient in 2005 (Figure 2) and average of the ten-year annual use was 161,056 pounds. Table 4 lists annual endosulfan use in the counties where the average annual use exceeded 1,000 pounds. The six top use counties where ten years average of annual use exceeded 6,000 pounds of active ingredient were Fresno, Kings, Imperial, Kern, Tulare, and Riverside in San Joaquin Valley and Imperial Valley (Figure 3). A side-by-side comparison of the use maps for 1997 and 2005 show decreased endofulfan use in 2005, mainly due to reduction of cotton crop in the San Joaquin Valley (Figure 4). Endosulfan use on cotton decreased 87% in 2005 vs 1997 in the top six counties.

Monthly use for the entire state showed that the peak use months were from June to September with some variations before year 2000 (Table 5). For the six top use counties, the peak use months were June to August in Fresno; June and July in Imperial; August and September in Kern; June to September in Kings; May to August in Riverside; and July to September in Tulare counties (Figure 5).

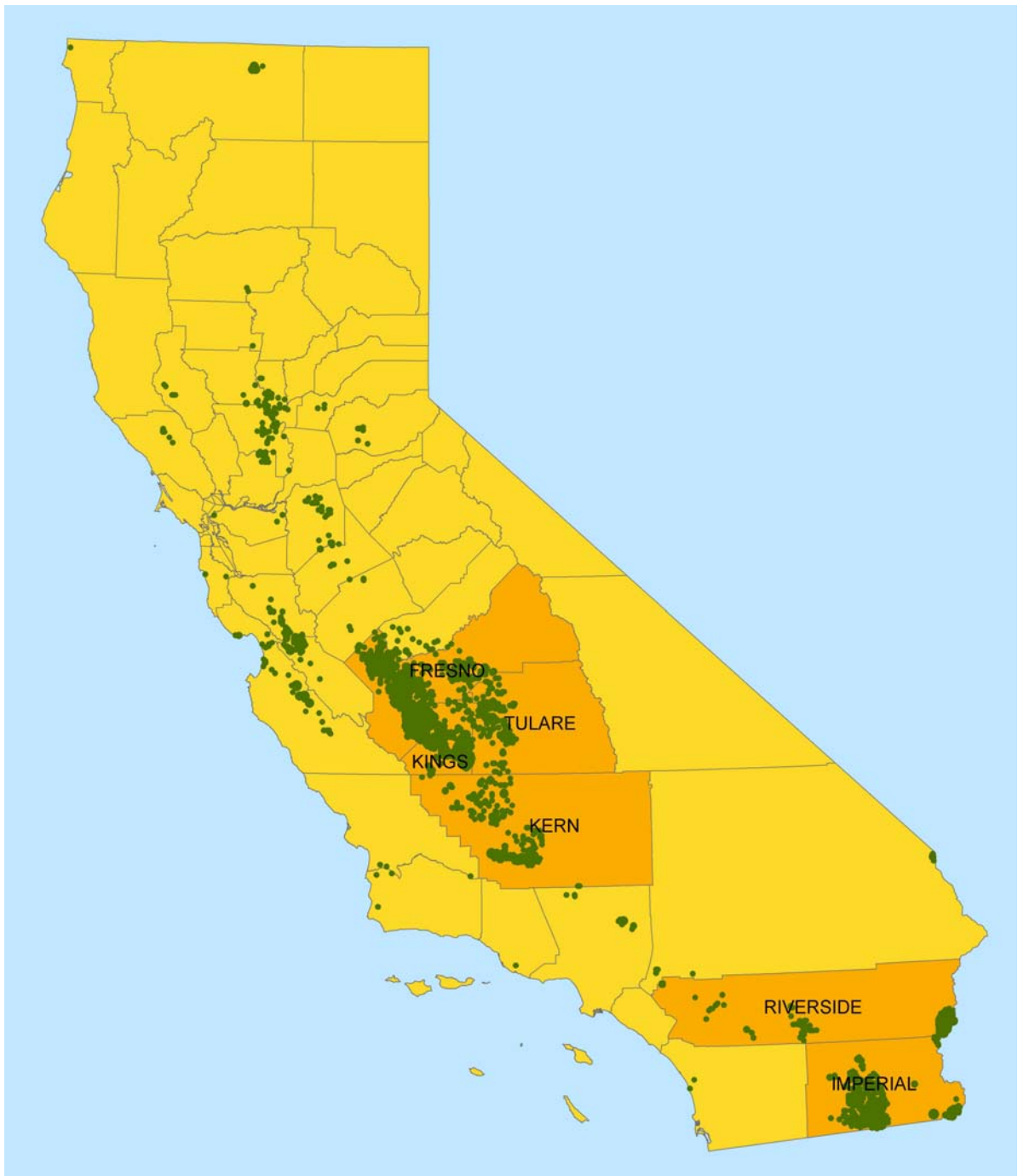
In California, endosulfan was mainly used on cotton, alfalfa, lettuce, tomato, melons, grapes, and various vegetables in the years between 1996 and 2005 (Table 6). For the six top use counties, the main use crops were head lettuce, alfalfa, canning tomatoes, and cotton in Fresno; alfalfa in Imperial; cotton and alfalfa in Kings, and cotton in Kern, Riverside, and Tulare counties (Figure 6).

A percentile comparison was performed to identify differences of individual endosulfan applications between 1997 and 2005. Although the absolute total pounds used and acreage applied in 2005 decreased to 1/3 of those in 1997, the individual application frequency distribution patterns for pounds used (Figure 7), acres applied (Figure 8), and application rates (Figure 9) were very similar. Generally, the relative differences of pounds used, acres applied, and application rates between 1997 and 2005 were less than 20% at each of five percentiles, 25, 50, 75, 90, and 95 (Figures 7-9), except for the pounds used (50%) and acres applied (40%) at 25 percentile (Figures 7 and 8). The top five crops for endosulfan use were cotton, alfalfa, lettuce head, canning tomato, and cantaloupe in both 1997 and 2005 (Table 6). It can be concluded that the use patterns of individual endosulfan applications were similar in 2005 compared to 1997.

**Figure 2. Reported endosulfan use from 1996 through 2005 (DPR PUR Database)****Table 4. Reported endosulfan use in counties with mean annual use >1,000 pounds**

County	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	Average
FRESNO	75400	104405	89624	100057	85684	83103	57991	51658	52220	43482	74362
KINGS	25296	49397	14181	18879	12883	9357	26293	20816	52302	14720	24412
IMPERIAL	68431	31165	24346	18481	17515	14830	6575	12406	4879	7282	20591
KERN	10125	21449	8917	4250	9399	25028	23534	26559	24750	2693	15670
TULARE	8427	8272	3756	3603	3673	8590	11384	7862	8206	1097	6487
RIVERSIDE	19956	9524	3394	2726	2604	2933	7605	8490	3046	4240	6452
SAN BERNARDINO	1853	264	528	17288	175	15		9			2013
MONTEREY	5007	3734	4438	2354	1609	224	140	1135	2	438	1908
SAN BENITO	2828	2911	1001	3829	1743	783	1081	614	2019	142	1695
YOLO	1143	359	900	1314	1593	1222	1193	1033	2265	2007	1303
SOLANO	6			2033	1457	1710	1798	579	1051	1720	1036

**Figure 3. Endosulfan use map**



**Figure 4. Comparison of endosulfan use during 1997 vs 2005 in the Central Valley**

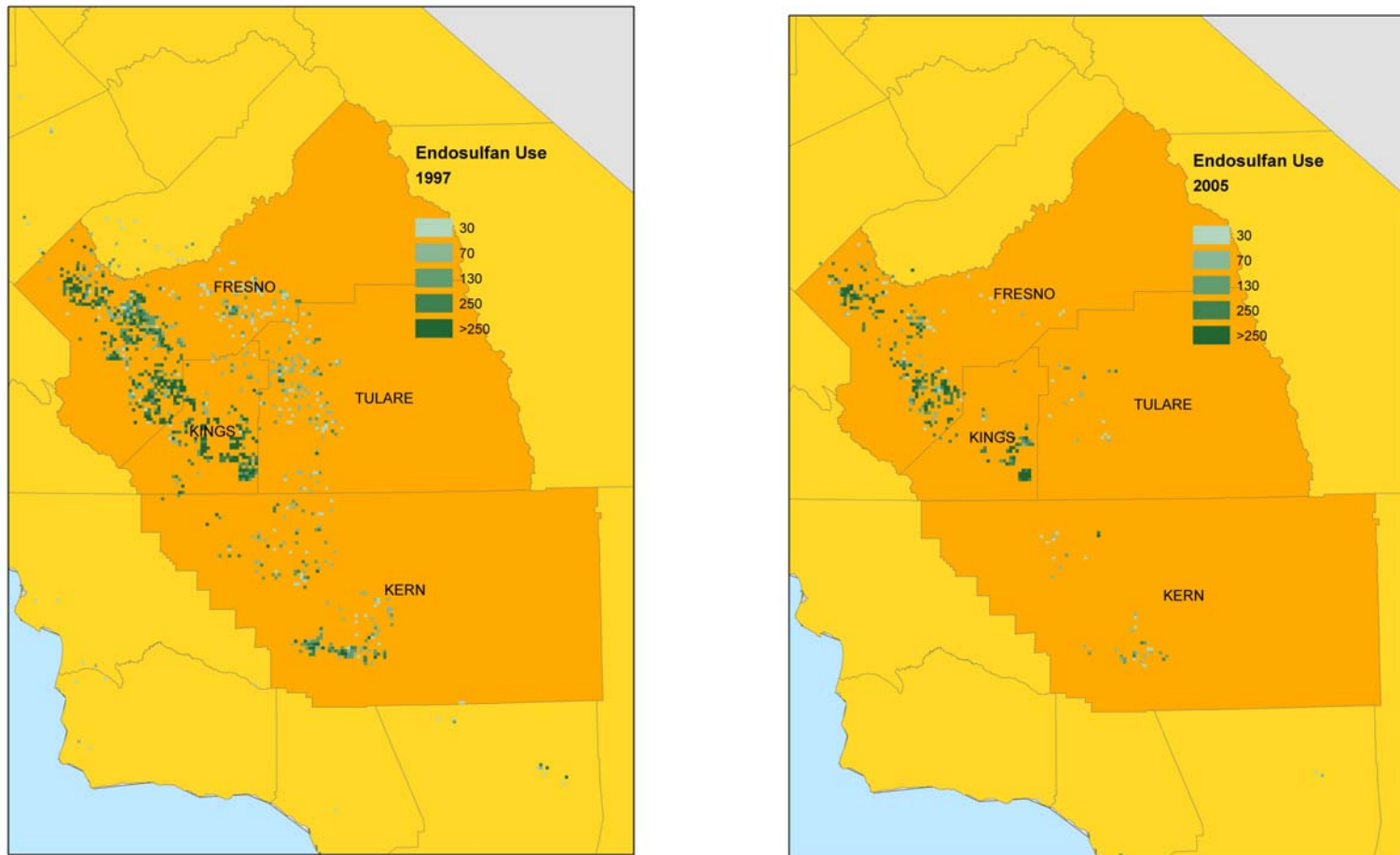
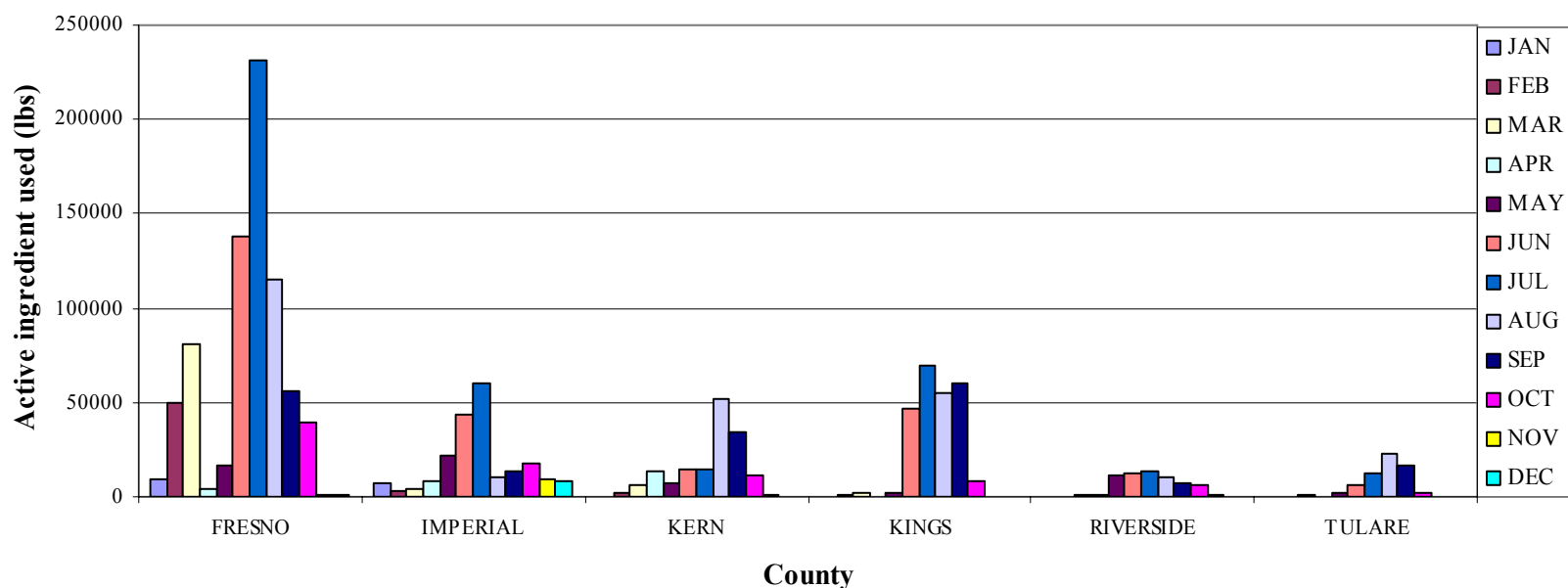


Table 5. Monthly reported endosulfan use from 1996 to 2005

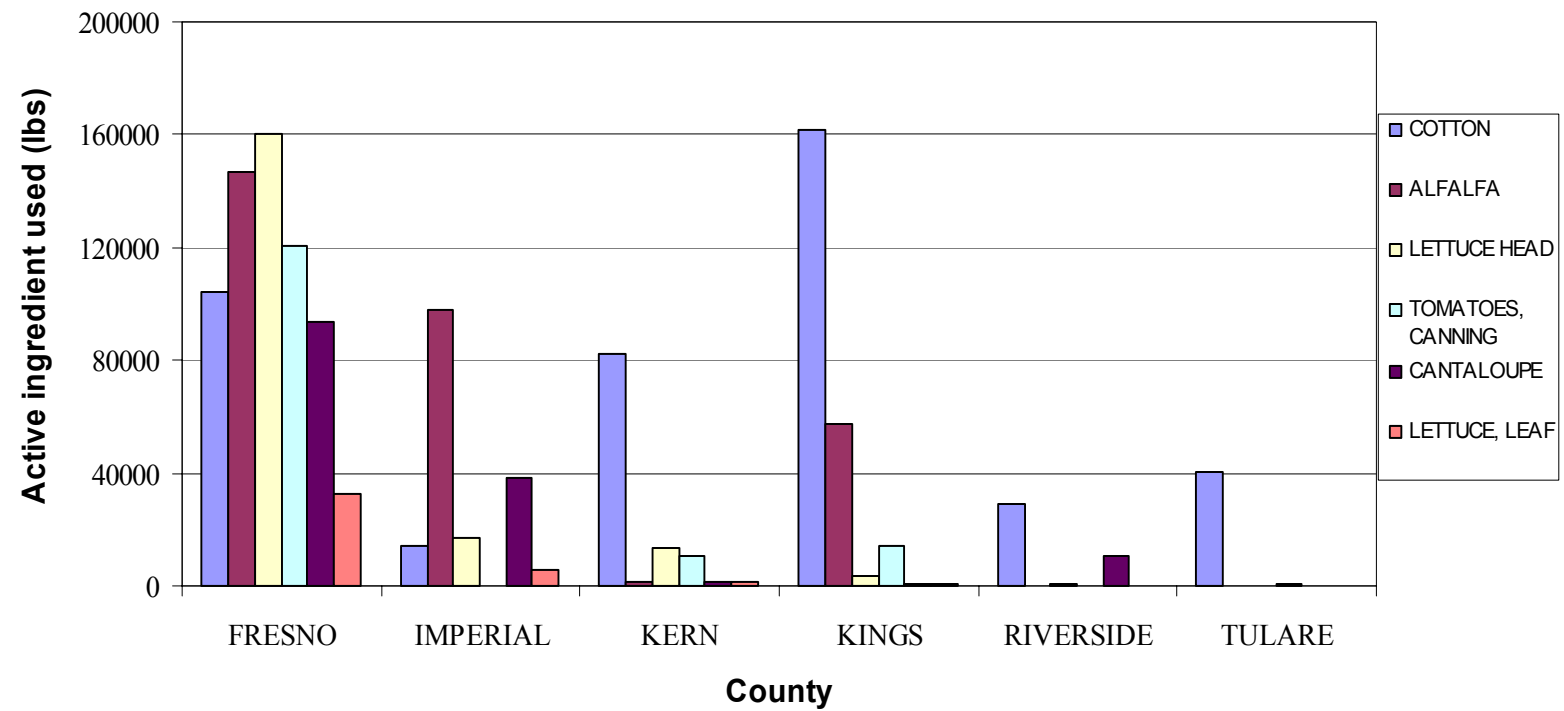
Month	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	Average
JAN	4369	2894	780	3992	821	1921	1649	843	838	346	18453
FEB	7001	7870	4257	4052	6901	7973	5797	6295	3094	4652	57891
MAR	8328	14577	14549	13961	8775	8878	6292	5927	7508	6902	95697
APR	10277	3904	5913	3248	2471	2840	6134	2078	849	691	38406
MAY	26640	14471	1537	22861	3198	7175	6333	1385	3044	3540	90183
JUN	37665	42264	17497	36382	42087	27737	13291	19147	14610	17205	267885
JUL	62505	90059	59212	55005	43556	29720	18966	20443	21559	20913	421938
AUG	33000	40342	29810	21653	20238	38742	26662	28355	48489	12797	300088
SEP	8179	9325	12175	13016	11900	21020	45779	35884	42097	7793	207169
OCT	12958	9430	8602	5478	4287	6906	10926	12617	10884	7387	89474
NOV	7212	2630	813	647	266	270	422	655	302	332	13547
DEC	5873	871	820	15	251	314	415	465	150	654	9828
Total	224007	238635	155963	180311	144751	153497	142666	134093	153424	83212	1610559

Figure 5. Monthly reported endosulfan use (1996-2005) in the top six counties



**Table 6. Reported endosulfan use for crops with mean annual use >200 pounds**

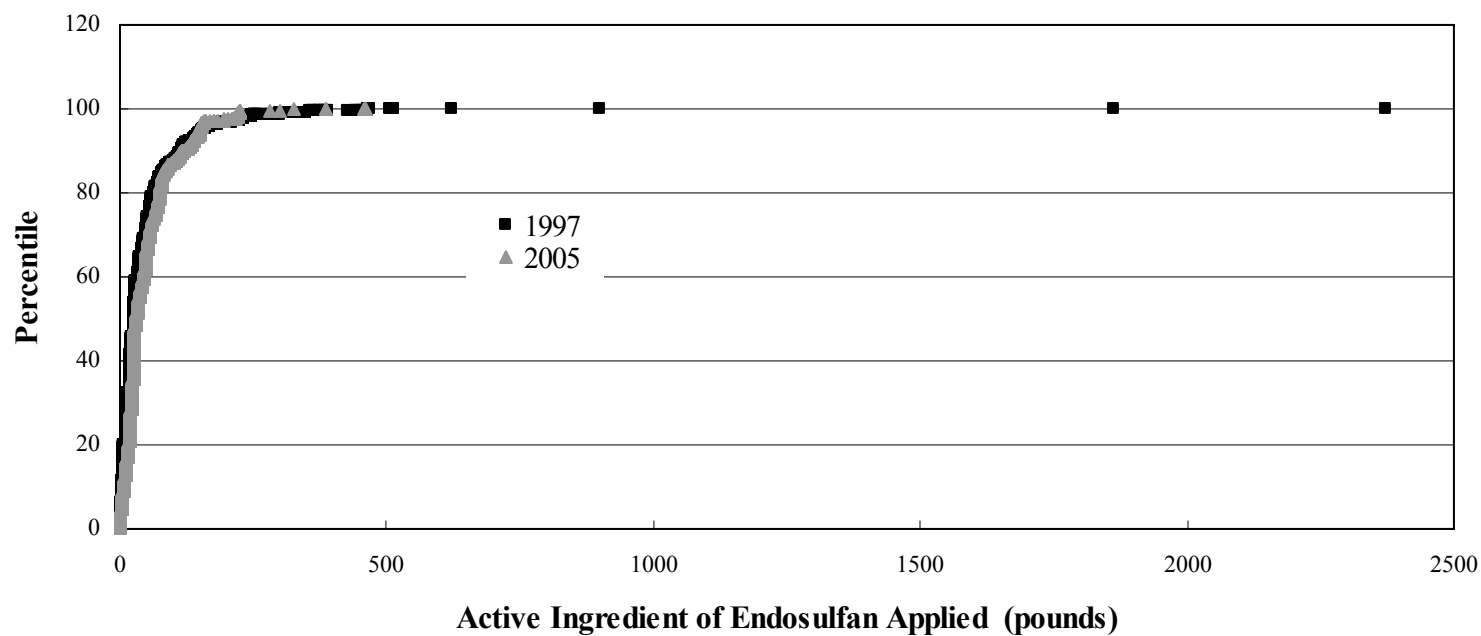
Commodity	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	Mean
COTTON	50525	91537	20784	7072	14136	44279	61320	58101	76638	11952	43634
ALFALFA	16440	39436	59726	63634	53175	25758	10198	12334	9603	13446	30375
LETTUCE, HEAD	24828	25839	22999	27922	17749	21133	15543	14833	17619	14444	20291
TOMATOES (CANNING)	19154	9005	9762	21383	21613	20802	14360	23254	20174	19302	17881
CANTALOUPE	42302	24988	12311	10631	11639	11800	8785	6927	9981	6053	14542
LETTUCE, LEAF	5975	6007	6054	7171	4900	5602	5106	4728	4324	4357	5423
GRAPES	9497	3767	2791	20799	3973	4310	2695	272	362	40	4851
MELONS	8036	6671	2409	1741	2783	2952	2703	2672	1013	1561	3254
BROCCOLI	4849	3322	5270	1958	1281	3326	2999	3590	3844	757	3120
PEPPERS, VEGETABLE	4511	1845	628	1005	1178	3125	322	1215	3885	1378	1909
CORN (HUMAN CONSUMPTION)	7001	1545	1306	1587	456	428	1839	319	274	1297	1605
SUGARBEET	5647	3310	147	1259	1649	332	2607		252		1520
WATERMELONS	3531	2403	374	991	959	888	2282	1615	1006	1096	1514
POTATO	2553	1987	130	1611	576	686	3264	470	1324	776	1338
TOMATO	2940	1388	1008	1981	2226	936	655	267	629	973	1300
BEANS (DRIED-TYPE)	1498	1268	952	2192	350	373	1576	380		368	896
WALNUT	3699	2408	286	636	358	287	30	80	707	81	857
PEACH	186	1048	168	820	1116	1010	946	73	51	14	543
CARROTS	607	1543	1075	205	163	644	129	374			474
APPLE	376	1469	768	492	656	5	343	446	52	111	472
CAULIFLOWER	910	701	570	683	494	485	256	112	50	25	429
PECAN	756	823	782	460	222	270	180		143	594	423
GRAPES, WINE	1093	749	731	376	23	103	465		135	103	378
STRAWBERRY	663	47	10	140	10	14		406	2	2330	362
PRUNE	262	188	851	175	513	222	492	329	187	298	352
NECTARINE	36	312	63	220	318	395	1201	72	52	16	268
RAPE	733	246	965	209	2			45			220
SQUASH	237	499	19	322	344	208	212	27	173	24	207
CABBAGE	555	260	275	195	118	234	30	145	118	109	204
CUCUMBER	261	362	16	368	87	710	158	1	0	73	204

**Figure 6. Reported endosulfan use (1996-2005) on the main crops in the top six counties**



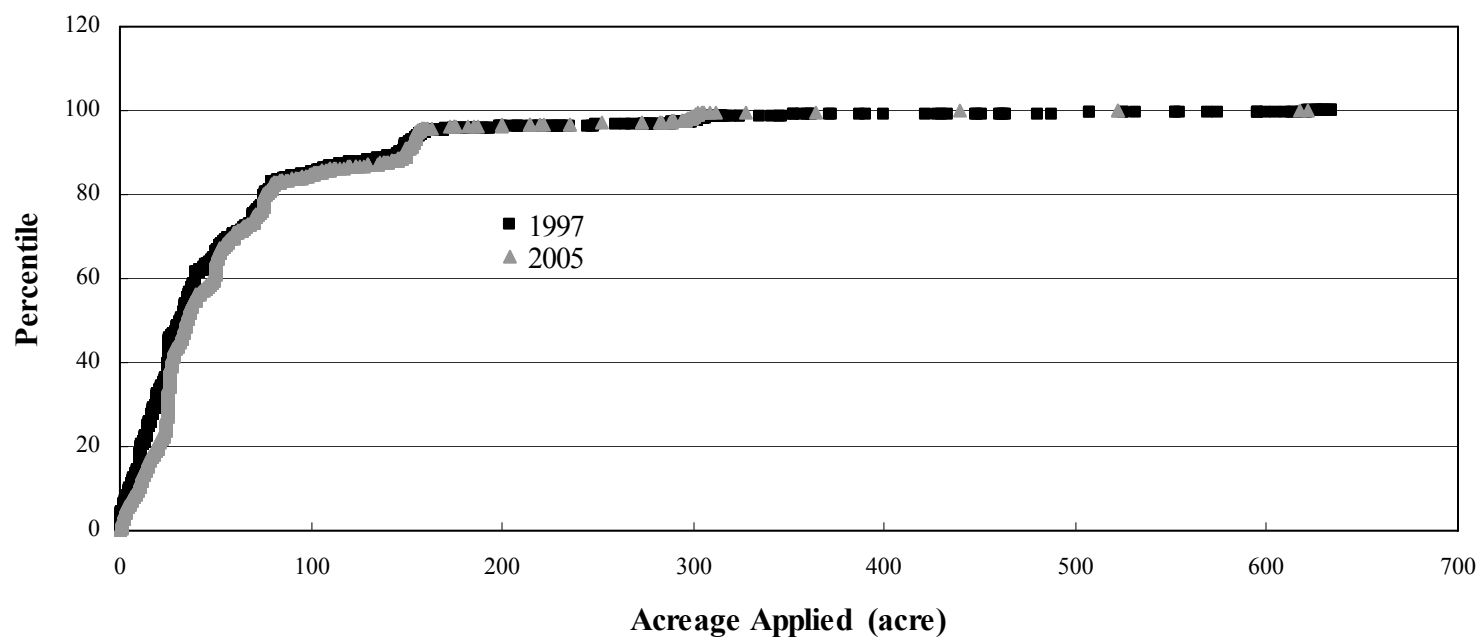
**Figure 7. Comparison of estimated percentile distribution for the pounds of individual endosulfan application in 1997 vs 2005**

Percentile	Pounds applied		Relative difference (%) (2005-1997)/average
	1997	2005	
25	12	20	50
50	26	30	14
75	56	66	16
90	116	120	3
95	148	150	1



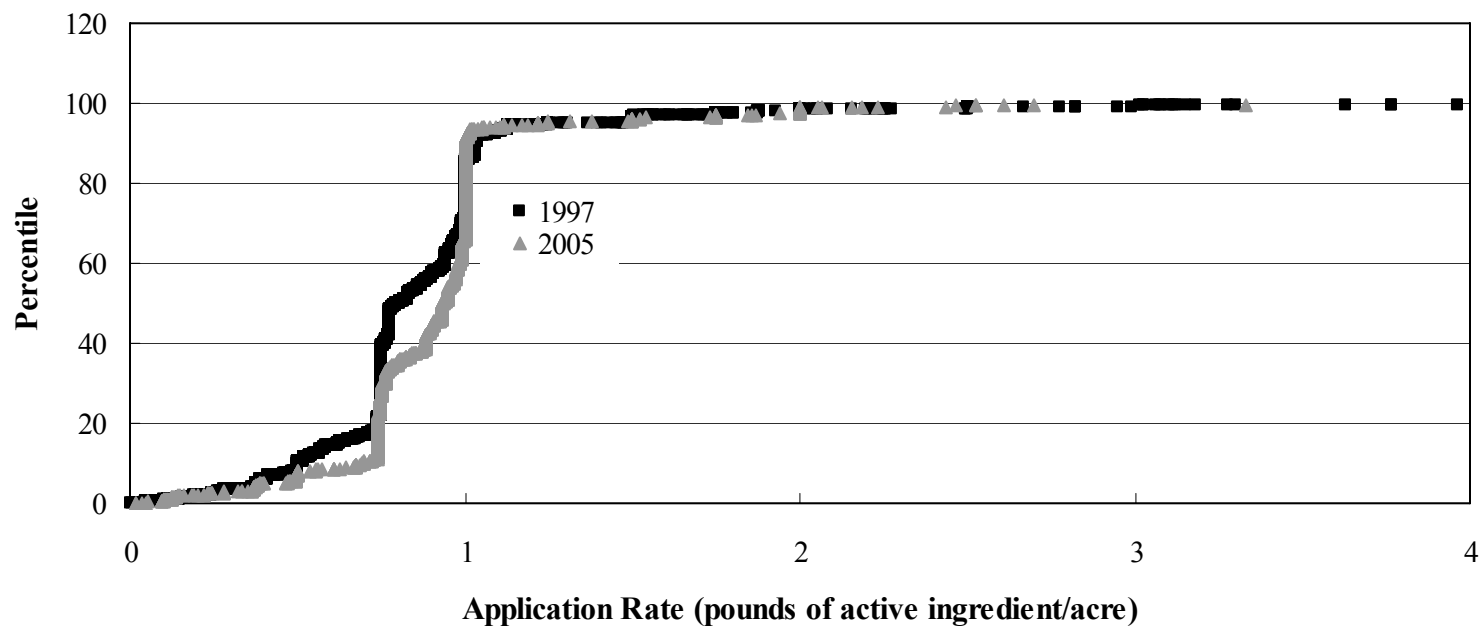
**Figure 8. Comparison of estimated percentile distribution for the acreage of individual endosulfan application in 1997 vs 2005**

Percentile	Acres applied		Relative difference (%) (2005-1997)/average
	1997	2005	
25	16	24	40
50	32	35	9
75	70	71	1
90	148	150	1
95	160	156	-3



**Figure 9. Comparison of estimated percentile distribution for the rate of individual endosulfan application in 1997 vs 2005**

Percentile	Application rate (pounds/acre)		Relative difference (%) (2005-1997)/average
	1997	2005	
25	0.75	0.75	0
50	0.80	0.93	15
75	1.00	1.00	0
90	1.04	1.00	-4
95	1.29	1.22	-6



## Environment Fate

The physicochemical properties of endosulfan determine its fate in environment. Endosulfan can be found in almost all media in the environment although it is released to the environment almost exclusively from pesticide application, and there are no known natural sources of endosulfan. The end-use product of endosulfan is a mixture of two isomers,  $\alpha$  and  $\beta$ , typically in a 2:1 ratio. The  $\alpha$ -isomer is more volatile and dissipative, while the  $\beta$ -isomer is generally more adsorptive and persistent (Rice *et al.*, 2002; US EPA, 2002). Its overall moderately volatile property (Lyman, et al., 1990) enables it to be transported as vapor and spray drift to multiple media, while its moderately adsorptive and persistency properties enable it to stay in the environment for an extended period and can be transported via runoff to surface water bodies or via dust dispersion to atmosphere and redeposit to different areas. Therefore, endosulfan has been detected in areas where it was not used, *e.g.*, the Lake Tahoe Basin and the Sequoia National Park (LeNoir, et al., 1999; McConnell, et al., 1998).

Endosulfan inter-environmental media transportation and intra-media transformation routes involve adsorption/desorption, volatilization, vapor transportation, spray drift, runoff, and abiotic and biotic degradation. Spray drift in this document refers to endosulfan off-site movement in air which occurs during the course of a spray application. Vapor transportation, spray drift, and runoff contribute largely to endosulfan movement from the application to off target areas. Adsorption contributes partially to endosulfan persistence. In general, adsorption reduces its potential mobility. However, the adsorbed endosulfan-soil colloid complex can be transported via runoff to surface water bodies or via dust dispersion to atmosphere and redeposit to off target areas. Significance of dust transport depends on many factors and mainly contributes to local transportation. Photolysis and subsurface leaching are negligible. An integrated modeling of these pathways for endosulfan regional transportation from a large cotton growing area to two main rivers in Australia showed that spray drift and vapor transport both contributed low-level but nearly continuous inputs to the riverine endosulfan load during spraying season; whereas runoff provided occasional but higher inputs. Dust transportation was found not important for regional endosulfan transport (Raupach, et al., 2001).

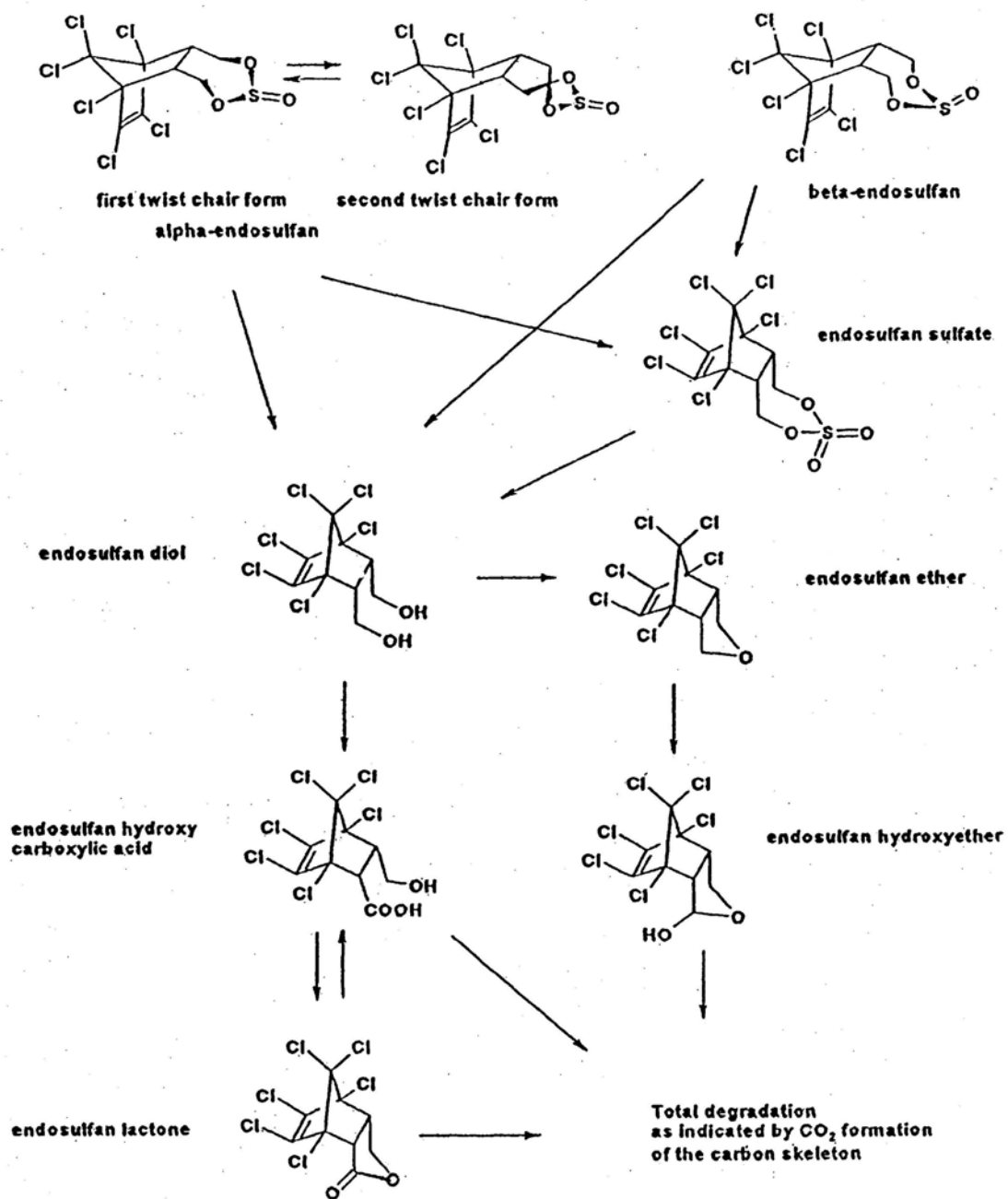
Endosulfan degradation can be abiotic or biotic processes in aerobic and anaerobic conditions. Oxidation and hydrolysis are the main processes for endosulfan degradation. Both  $\alpha$ - and  $\beta$ -endosulfan can be oxidized to endosulfan sulfate via biotic metabolism. Endosulfan sulfate is of comparable toxicity as its parents and more persistent with half-life of 100-150 days, two or more times longer than its parents (Table 2). Estimated half-lives for the combined toxic residues ( $\alpha$ - and  $\beta$ -endosulfan plus endosulfan sulfate) range from 9 months to 6 years (US EPA, 2002). They all can, when in water, hydrolyze abiotically or biotically to endosulfan diol. Endosulfan diol is more hydrophilic and less toxic. The open chemical structure of endosulfan diol may close to form endosulfan ether or oxidize to endosulfan hydroxyl carboxylic acid. Further reaction converts endosulfan ether to endosulfan hydroxyether, which can eventually be mineralized to release carbon dioxide. Endosulfan hydroxyl carboxylic acid may be directly mineralized, or close the ring and form endosulfan lactone. The endosulfan hydroxylcarboxylate and endosulfan lactone conversions are reversible processes depending upon redox potential, pH, and/or microbial population of the local environment. They all can eventually be mineralized to release carbon dioxide (Figure 10). However, microbial mineralization is generally slow (GFEA, 2004). In a

modular estuarine mesocosm study, it was found the first time that  $\gamma$ -hydroxycarboxylate was formed from endosulfan lactone. However, no further oxidation was reported and  $\gamma$ -hydroxycarboxylate was claimed as a terminal degradation product in this 100-hour study (Walse, et al., 2003). In general, the most prevailing degradation product is endosulfan sulfate, followed by endosulfan diol, and other degradation products.

Endosulfan microbial degradation has been extensively studied in soils, soil inocula, mixed microbial cultures, and isolated microorganisms for intoxicant remediation (Kathpal, et al., 1997; Rao and Murty, 1980; Guerin, 1999; Miles and Moy, 1979; Schneider and Ballschmiter, 1995; Awasthi, et al., 1997; El Zorganir and Omer, 1974; Katayama and Matsumura, 1993; Kullman and Matsumura, 1996; Martens, 1976; Mukherjee and Gopal, 1994; Sutherland, et al., 2000, 2002a, 2002b, 2002c; Kim, et al., 2001; Hussain, et al., 2007; Shivaramaiah and Kennedy, 2006; Shetty, et al., 2000; Siddique, et al. 2003). In a study on 28 soil fungi, 49 soil bacteria, and 10 actinomycetes for testing their ability to degrade  $^{14}\text{C}$ -labeled endosulfan, 16 fungi, 15 bacteria, and 3 actinomycetes were found capable of metabolizing more than 30% of the applied endosulfan. The major metabolites detected were endosulfan sulfate, formed by oxidation of the sulfite group, and endosulfan diol, formed by hydrolysis of the ester bond (Martens 1976). In general, endosulfan is a poor biological energy source, as it contains only six potential reducing electrons. Attempts to enrich for endosulfan-degrading microorganisms using endosulfan as a carbon source were unsuccessful (Sutherland, et al., 2000; Guerin, 1999). However, endosulfan has a relatively reactive cyclic sulfite diester group (Van Woerden, 1963) for initial microbial degradation.

The enzymes involved in endosulfan metabolism by fungus and bacterium were investigated in different conditions. Generally, soil fungi have been shown to metabolize endosulfan favoring an oxidative enzyme system and resulted in a major metabolite of endosulfan sulfate, whereas soil bacteria are favoring hydrolysis enzyme system to metabolize endosulfan and produce predominantly endosulfan diol (Martens, 1976).

Figure 10. Endosulfan degradation in soil and water (source: GFEA, 2004)



## **Fate and persistence in soil**

### ***Adsorption and desorption***

A main process of endosulfan in soil is adsorption/desorption. When endosulfan is applied to soil in aqueous solution, it is adsorbed onto and desorbed from soil colloidal particles towards a dynamic equilibrium with soil aqueous solution concentration. An average adsorption coefficient  $K_{oc} = 12,000 \text{ cm}^3/\text{g}$  (Table 2) indicates moderate affinity to soil colloidal particles. Adsorption isotherm studies with concentration ranging from 0.02 to 0.16 mg/L in four soils indicated that  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate had similar adsorption affinities to the studied soils with average  $K_{oc}$  of  $10,600 \pm 2100$  and  $13,500 \pm 2600 \text{ cm}^3/\text{g}$  for  $\alpha$ - and  $\beta$ -endosulfan, respectively, and  $K_{oc}$  ranged from 5,700 to 11,400  $\text{cm}^3/\text{g}$  for endosulfan sulfate and 720 to 1200  $\text{cm}^3/\text{g}$  for endosulfan diol (Goerlitz and Eyrich, 1987a, 1987b).

### ***Runoff transportation and leaching***

Endosulfan dissolved in soil solution and adsorbed on soil particles can also be transported by runoff, via rainfall during storm events and agricultural irrigation, to rivers and lakes, and eventually to the ocean. This is a main route contributing to endosulfan off-target movement. It will be further discussed in the regional transportation section.

Moderate adsorption of endosulfan is expected to have low potential to leach to ground water. It can persist for weeks to months after application, especially in acidic soils where hydrolysis is not favored. In addition, the endosulfan oxidation degradate, endosulfan sulfate, is more persistent than the parent isomers. In three terrestrial dissipation studies with or without crop cultivation conducted in Georgia and California, maximum leaching did not exceed 66 cm in any cases studied. U.S. EPA concluded that “the potential for endosulfan to reach ground water is limited to acidic to neutral soils and aquifers where preferential flow may be a prevalent pathway to ground water or where the ground water is shallow and is overlain by highly permeable soils”. Vulnerable aquifers below acidic soils can be prone to contamination (U.S. EPA, 2002).

Endosulfan loss from agricultural fields via runoff and leaching depends on many factors, such as soil texture, organic matter content, rainfall intensity, and water table level, etc. A laboratory study was conducted using stainless-steel runoff-leaching chambers for measuring effects of soil type, rainfall intensity, and water table depth on endosulfan loss via runoff and leaching (Zhou, et al., 2003). Two agricultural calcareous soils, a gravelly loam (coarse) with pH of 7.96, organic carbon of 14.9% and a loam (fine) with pH of 8.18, organic carbon of 19.6%, were packed to a 14 cm depth in two individual chambers tilted with slope of 3°. Water table depth was set at three levels for the coarse soil and one for fine soil. Artificial rainfall intensity was set at two levels for both soils. Results showed that endosulfan losses were the greatest in runoff sediment, followed by runoff water, and then leachate in all studied conditions except one when rainfall was at the lowest intensity (75 mm/hour) in the fine soil (Table 7). In this case, runoff did not occur and leaching was the highest among the treatments, about 2% of applied endosulfan. This study also indicated that both higher rainfall intensity and higher water table significantly increased both  $\alpha$ - and  $\beta$ -endosulfan losses from runoff. Although this study did not attempt endosulfan mass balance with volatile and degradation of endosulfan, the relative results suggested that agricultural management practice to prevent surface runoff, especially for runoff sediment, would reduce endosulfan being transported to off-target areas.

**Table 7. Endosulfan losses via runoff and leaching in different conditions\***

Soil type	Water table depth	Rainfall intensity	Runoff water		Runoff sediment		Leaching	
	Cm	mm/hour	% of applied endosulfan					
			$\alpha$	$\beta$	$\alpha$	$\beta$	A	$\beta$
Very gravy loam (coarse)	4.5	150	5.12	4.23	12.90	13.70	0.06	0.04
	9.5	150	4.87	4.07	7.14	8.80	0.19	0.16
	>14	150	3.14	2.77	2.92	3.71	0.57	0.50
	>14	75	0	0	0	0	2.37	2.01
Loam (fine)	>14	150	7.36	5.76	28.70	29.60	0.03	0.03
	>14	75	2.44	1.59	6.92	6.95	0.05	0.03

\*adapted from Zhou, et al., 2003.

Research shows that plastic polyethylene mulch, a common vegetable production practice, may increase runoff loss of endosulfan and other pesticides. The research compared the plastic mulch with vegetative hairy vetch mulch in a field plot study (Rice, et al., 2001). The results summarized in Table 8 showed a significantly greater endosulfan loss due to larger volumes of runoff water collected from plots with plastic mulch than vegetative mulch ( $p \leq 0.05$ ). Larger runoff volume resulted in greater soil erosion and increased off-target loading of both dissolved and particle bound endosulfan. Comparable results were reported in another study that compared polyethylene mulch with bare soil (McCall et al., 1988). These studies suggest that alteration of current vegetable production practice can reduce adverse effect of off-target endosulfan due to runoff transportation.



**Table 8. Comparison of plastic and vegetative mulches on runoff transportation of endosulfan\***

		Plastic mulch		Vegetative mulch	
		Range	Mean $\pm$ SD	Range	Mean $\pm$ SD
<b>Runoff concentration</b>					
Dissolved in water ( $\mu\text{g/L}$ )	$\alpha$ -endosulfan	0.33-10.68	1.70 $\pm$ 1.31	0.05-33.89	0.94 $\pm$ 1.86
	$\beta$ - endosulfan	0.41-27.90	2.59 $\pm$ 1.31	0.05-4.67	0.67 $\pm$ 1.81
Adsorbed on particle ( $\mu\text{g/g}$ )	$\alpha$ -endosulfan	0.01-14,339	9.43 $\pm$ 5.17	0.01-23,200	14.61 $\pm$ 5.12
	$\beta$ - endosulfan	0.06-14,722	27.05 $\pm$ 5.00	0.13-35,666	35.46 $\pm$ 5.01
<b>Runoff load</b>					
Dissolved in water ( $\mu\text{g/m}^2$ )	$\alpha$ -endosulfan	0.40-227	10.90 $\pm$ 1.86	0.04-147	1.50 $\pm$ 2.25
	$\beta$ - endosulfan	0.12-714	14.39 $\pm$ 2.65	0.07-19.5	1.19 $\pm$ 2.00
Adsorbed on particle ( $\mu\text{g/m}^2$ )	$\alpha$ -endosulfan	0.09-1,150	6.67 $\pm$ 2.01	0.04-279	3.11 $\pm$ 2.60
	$\beta$ - endosulfan	1.03-1,180	24.74 $\pm$ 2.20	0.10-412	0.67 $\pm$ 1.81
Total load ( $\mu\text{g/m}^2$ )	$\alpha$ -endosulfan	0.79-1,377	17.57 $\pm$ 3.87	0.08-420.4	2.78 $\pm$ 4.96
	$\beta$ - endosulfan	0.24-1,893	39.13 $\pm$ 4.85	0.48-423.2	4.30 $\pm$ 4.60

\*adapted from Rice, et al., 2001

#### ***Volatilization and dust transportation***

Endosulfan can volatilize to the atmosphere from soil water surface. Volatilization from a source is driven by Henry's Law constant of a chemical. Approximately half of the amount of  $\alpha$ - and  $\beta$ -endosulfan applied to surface soils in Queensland and New South Wales, Australia, dissipated via volatilization in 3-5 and 5-8 days, respectively (Leys, et al., 1998). Even heavy rains from the first to third day after endosulfan application to freshly tilled soil could not prevent 34.5% and 14.5% losses from soil due to volatile flux of  $\alpha$ -endosulfan and  $\beta$ -endosulfan, respectively, within 20 days (Rice, et al., 2002). The majority, 78%, of the volatile flux loss occurred within 4 days of treatment.

Endosulfan bounded on soil particles may also be transported by dust from dry soils. Fine particulate dust can be uplifted by wind, turbulence, and traffic or agricultural operations and transported locally by wind or to a short distance, and deposited onto off-target areas. These will be discussed in the atmospheric transportation section.

#### ***Degradation***

Endosulfan degradation in soil involves both abiotic and/or biotic processes. Degradation rate varies depending on many factors, such as soil type, organic carbon content, pH, temperature, moisture content, microbial population and biomass, etc. Abiotic hydrolysis is an important degradation route in neutral to alkaline aqueous soil solution. Half-lives vary significantly depending on pH values (Table 16). The ability of soil mineral surfaces to catalyze the hydrolysis of  $\alpha$ -endosulfan and the effects of organic matter on hydrolysis were investigated in laboratory study at 25 °C and pH 8 (Hengpraprom, et al., 2002; Hengpraprom, 2004).  $\alpha$ -

endosulfan was incorporated in two soil clay mineral suspensions, kaolinite and montmorillonite, with or without amendment with three types of typical soil humic acids for up to 48 hours, and adsorption isotherms were determined for both  $\alpha$ -endosulfan and its hydrolysis product, endosulfan diol. The Freundlich sorption coefficient,  $K_f$ , demonstrated a greater sorption of  $\alpha$ -endosulfan on montmorillonite than kaolinite. Endosulfan diol showed less adsorption on both minerals. Compared to the water-only control, montmorillonite likely catalyzed  $\alpha$ -endosulfan hydrolysis, but kaolinite delayed the hydrolysis. The effects of each of the three humic acids amended onto each of the two clay minerals were different probably due to their different polarity and complexity of the humic acid-mineral interfaces. Effect of organic matter on endosulfan biodegradation was studied in laboratory containers (Al-Hassan, et al. 2004). Four treatments of four different sources of organic matter, poultry by-product meal, poultry manure, dairy manure, and municipal solid waste compost were added to the potted soil. The half-life of  $\alpha$ -endosulfan in the poultry by-product meal treatment was 15 days, but 22 days in the other treatments. The half-life of  $\beta$ -endosulfan was 22 days in the poultry by-product meal treatment and followed a two-phase pattern, and 57 days in the municipal solid waste compost treatment. For the other two treatments, the half-life of  $\beta$ -endosulfan was estimated, by extrapolation, about 115 days.

When the pH value is less than 7, both  $\alpha$ - and  $\beta$ -isomers are persistent to hydrolysis (US EPA, 2002). Microbial oxidation becomes the predominant degradation route. Half-lives in acidic to neutral soils range from one to two months for  $\alpha$ -endosulfan and from three to nine months for  $\beta$ -endosulfan under aerobic conditions (Table 9). Endosulfan sulfate is the main degradation product by oxidation in aerobic soils while endosulfan diol is mainly formed by chemical or biological hydrolysis in anaerobic soils (US EPA, 2001).

**Table 9. Soil degradation half-lives (days)**

Conditions	Range			Typical	References
Field				50	EXTOXNET, 2007
Field (aerobic)	75-110				GFEA, 2004
Fields in UK	62-126 (summer), 68-87 (fall)				Footprint, 2007
Laboratory (4 soils, aerobic)	117-391				GFEA, 2004
Laboratory (20 °C)	28-50				Footprint, 2007
	$\alpha$ -isomer	$\beta$ -isomer	$\alpha$ - and $\beta$ -endosulfan	$\alpha$ -, $\beta$ -, and sulfate endosulfan	
5 Soils (pH 5-7, aerobic)	35-67	104-265	75-125	288-2148	US EPA (2001)
2 Soils (pH 6-7 anaerobic)	105-124	136-161	144-154		US EPA (2001)

Photodegradation of endosulfan on soil surfaces is not an important process. Half-lives have been reported to be greater than 200 days under simulated and natural light conditions (GFEA, 2004). A 30-day study on a pH 6.4 silt loam soil indicated that both  $\alpha$ - and  $\beta$ -endosulfan were stable to natural sunlight (US EPA, 2001).

A study in New South Wales, Australia (Kennedy, et al., 2001) looked at overall mass balance of endosulfan field dissipation. Approximately 70% of the endosulfan dissipation occurred via volatilization from cover crop and soil surface, and mostly as  $\alpha$ -endosulfan. Only a small portion, 8.5% remained on field a month after the last spraying. Of this portion 95% was in soil and 5% on cotton plants. Endosulfan losses through runoff during the entire growing season accounted for less than 2% of the total pesticide applied. Degradation in plants and soil microorganisms were responsible for degradation of approximately 25% to 30% of the total endosulfan applied. By the start of the following spraying season, only 1% of the initially applied endosulfan remained in the soil, mostly as endosulfan sulfate, and there was very little residue build-up between years in this study.

Overall soil degradation rates observed in the field studies varied in order of magnitude depending on soil and other environmental conditions. In the three terrestrial dissipation studies with or without crop cultivation conducted in Georgia and California (US EPA, 2001), half-lives varied from 6-71 days for  $\alpha$ -isomer, 23-106 days for  $\beta$ -isomer, 41-93 days for combined  $\alpha$ - and  $\beta$ -isomers, and 97-172 days for total endosulfan residues. Kennedy, et al. (2001) found that endosulfan dissipation from both foliage and soil was best explained by a two-phase process. Half-lives of total endosulfan toxic residues ( $\alpha$ - and  $\beta$ -endosulfan and the sulfate product) in the first phase were 1.6 days in foliage and 7.1 days in soil, mainly due to the rapid volatilization of the parent isomers in the first 5 days. In the second phase, half-lives were 9.5 days in foliage and 82 days in soil, mostly due to the persistence of the degradation product, endosulfan sulfate. Concentration of endosulfan residues in runoff water varied from 2.5 to 45 mg/L depending on residue levels in soils at the time of the irrigation or storm events. The residue levels in soils varied depending on application rates, application interval, field crop coverage, and microbial degradation. In addition, a terrestrial field study was conducted on bare cotton soil under sub-tropical conditions of northern India during 1989-1990 (Kathpal, et al., 1996). Endosulfan was sprayed at 875 g/ha, 42 and 63 days after the assumed date of sowing in two separate treatments. Soil samples were collected periodically from different depths of the soil profiles. Dissipation by 92-97% of the total endosulfan occurred in the first four-weeks and by about 99% in 238 days in two distinct phases of first-order kinetics. The parent compounds were metabolized to endosulfan-diol and endosulfan sulfate. Endosulfan-diol remained confined in the upper 5-cm layer and dissipated completely in 28 days; whereas endosulfan sulfate was first detected seven days after treatment and persisted until the end of the experiment, remaining confined in the upper 0-10 cm of the soil profile. The  $\beta$ -isomer also did not leach down beyond 10 cm depth.

Half-lives of endosulfan degradation in anaerobic soils are longer than those in aerobic soils. In laboratory experiments, endosulfan half-lives was determined in four treatments, with or without flooding and with or without straw amendment (Sethunathan, et al., 2002). Results are summarized in Table 10. Endosulfan sulfate showed recalcitrant to further degradation under both water treatments irrespective of organic matter amendment.

**Table 10. Comparison of half-lives under aerobic and anaerobic conditions**

<b>Flooded</b>	<b>Straw amended</b>	<b>Half-life (days)</b>
No	No	137
No	Yes	125
Yes	No	430
Yes	Yes	501

### **Fate and persistence in atmosphere**

#### ***Volatilization from crop surface and soil solution***

Volatilization and vapor transportation are the main processes for endosulfan entering to and moving in atmosphere. When endosulfan is applied via spray onto crops, vapor transport begins with volatilization from the crop surface. The vapor is dispersed by atmospheric wind and turbulence, and deposited on downwind surfaces, including soil, waterways, crops, building, etc. The continuous volatilization and vapor transportation eventually removed up to 50%-70% of the total endosulfan deposited on crop surfaces during a spray (Rüdel, 1997; Rice et al., 1997). Briggs, et al. (1998) measured significant levels of endosulfan in air a day or two after a crop was sprayed due to volatilization from the crop surface. In laboratory wind tunnel experiments at a constant airflow of 1 m/s, temperature of 21- 22 °C, and relative air humidity of 50%, approximately 25-30% of the endosulfan dissipated from soil to air over a period of 24 hours (Rüdel, 1992a and 1997). 64% of the applied endosulfan eroded from bean leaves under these experimental conditions (Rüdel, 1992b). These results suggested that soil adsorption was more competitive to volatilization than foliar absorption or penetration. However, volatilization of endosulfan sulfate was much lower than its parent endosulfan isomers, about 5% released to the atmosphere from plant surfaces within 24 hours. Volatilization from soil solution and free water surface also contribute to atmospheric endosulfan concentrations and activities, but at much lower rates, 5 to 13 folds lower from soil compared to plants (Rüdel, 1997).

Volatilization is strongly affected by temperature. In a field experiment with a mean maximum temperature of 40°C in a 48-hour period, half-lives for  $\alpha$ - and  $\beta$ -endosulfan dissipation from cotton foliage following application were 12 hours and 36 hours, respectively. At a mean maximum temperature of 29°C, the half-lives increased to 24 and 60 hours, respectively (Ahmad, et al., 1995).

#### ***Spray drift***

Spray drift from endosulfan applications can result in endosulfan unintentionally moved to off-target areas. In 1988, after endosulfan residue was detected in bay mussels collected from Elkhorn Slough (Stephenson, et al., 1980; Hayes and Phillips, 1984), the California Department of Food and Agriculture monitored aerial applications of endosulfan to three artichoke fields in the Moss Landing drainage area of Monterey County. Endosulfan concentrations were found on deposition samples located 18 feet (5.5 meters) from the application field borders (Fleck, et al., 1991). This information was used in developing mitigation measures to reduce off-site movement of endosulfan (Okumura, 1991 and 1992).

Spray drift is manageable via regulations and technique improvement. Regulations include restrictions of weather conditions and buffer zone for aerial applications. To mitigate spray drift, US EPA has been enforcing a 300-foot buffer zone between treated areas and water bodies for aerial applications since 1991. California has issued more restrictions for endosulfan use (Okumura, 1991 and 1992).

Technical improvement can be made via adapting application methods and techniques via adjusting aircraft flight height and speed, and adapting nozzle type and droplet size. A series of field studies on spray drift from endosulfan applications were conducted on Australian cotton farms during 1993-1998. These studies included single flight-line drift tests to determine the effects of spray nozzle type and droplet size on airborne drift profiles. The water-based endosulfan was applied using hydraulic CP nozzle at 30° deflector setting with volume median diameter of 182  $\mu\text{m}$ ; while oil-based endosulfan was applied using Microair AU5000 nozzles at 4000 rpm with volume median diameter of 67  $\mu\text{m}$ . The results showed that deposition 500 meters downwind of the field boundary and over a wide range of weather conditions, cotton crop leaf variations, and application techniques, averaged approximately 2% of the field application rate with oil-based endosulfan applications and 1% with water based applications. Mean airborne drift values measured using towers placed 100 meters downwind were a third as much with water-based endosulfan applications compared with oil-based applications. However, selection of large droplet placement with volume median diameter about 250  $\mu\text{m}$  was required to ensure that droplet numbers per unit leaf area were sufficient for pest control efficacy (Woods, et al., 2001).

### ***Dust transportation***

Besides volatilization and spray drift, dust dispersion and transportation can contribute to atmospheric endosulfan activities. Its importance depends on regional weather, geography, and topography conditions, and anthropogenic activities. Dust transport can carry all three forms of endosulfan,  $\alpha$ -isomer,  $\beta$ -isomer, and endosulfan sulfate, but much lower in magnitude than either spray drift or vapor transport. Australian scientists carefully measured airborne dust and reported that the mass fractions of total endosulfan ( $\alpha$ -isomer,  $\beta$ -isomer, and endosulfan sulfate) were about 1 ppm for dust uplifted from unpaved roads by vehicle traffic and about 1.8 ppm for dust uplifted from fields by cultivation (Leys *et al.*, 1998). The mass fraction for dust uplifted by regional-scale wind erosion would certainly be lower because of dust dilution. The regional dust deposition rate measured a few hundred meters from a cotton farm was around 2 g-dust/ $\text{m}^2$  - month, incorporating dust from all sources (Leys *et al.*, 1998). Higher dust deposition rates were observed close to sources on-farm, but this short-range dust transport only relocated endosulfan on-farm. Based on these measurements and assuming all of monthly regional dust deposition occurring in a single event each month at 2 g-dust/ $\text{m}^2$ , modeling for endosulfan moving from a cotton farm to rivers estimated that endosulfan deposition by dust transport was  $2 \times 10^{-6}$  and  $1 \times 10^{-6}$  g/ $\text{m}^2$  for  $\alpha$ - and  $\beta$ -isomer, respectively, nearly 1000 fold lower than that by a typical endosulfan spray drift,  $1.4 \times 10^{-3}$  and  $0.72 \times 10^{-3}$  g/ $\text{m}^2$  for  $\alpha$ - and  $\beta$ -isomer, respectively (Briggs, et.al. 1998). Therefore, dust transportation is not a major route of movement for endosulfan regional transport.

### ***Degradation***

Endosulfan is not susceptible to atmospheric degradation. Neither abiotic hydrolysis nor photolysis is a significant process for endosulfan in the troposphere. Abiotic hydrolysis is

avored in neutral to alkaline conditions as discussed previously. Cloud droplets and rainwater usually, as a consequence of atmospheric carbon dioxide content and naturally occurring trace substances, have pH values 4-6 (GFEA, 2004). Therefore, hydrolysis is not a common process of endosulfan degradation in the atmosphere.

Photolysis degradation can also be negligible. Endosulfan does not absorb solar radiation of the troposphere and its spectrograph showed no sorption within visible light range (Stumpf and Schink, 1988). However, indirect photo-oxidation with OH-radicals may contribute to removal of endosulfan from the troposphere. Estimated half-life was  $27 \pm 11$  days for  $\alpha$ -endosulfan based on a direct measurement study in a gas-phase reaction chamber at 75 °C and an aerial [OH] concentration of  $5 \times 10^5/\text{m}^3$  (Zetzsch, 1992).  $\beta$ -endosulfan was not accessible to this technique because of its lower volatility. In an indirect measurement using toluene as a reference, estimated half-lives were  $>2.7$  days for  $\alpha$ -endosulfan (Kloepffer, 1992a),  $>15$  days for  $\beta$ -endosulfan (Kloepffer, 1992b), and minimum 2.7 days for endosulfan sulfate (Kloepffer, 1992c). While both endosulfan isomers are resistant to photodegradation, their metabolites endosulfan sulfate and endosulfan diol are susceptible to photolysis (WHO, 1988). However, endosulfan degradates are not abundant in the atmosphere.

#### *Air concentrations*

Endosulfan concentration in air is dependent on the distance from the application site. For short-range transportation, seasonal variations typically mirror the agricultural application period. In a predominantly agricultural region of the Delmarva Peninsula in the east coast,  $\alpha$ -endosulfan was detected in 97% of weekly air samples ( $n=129$ ) in 2000-2003. Concentrations exhibited a lognormal distribution with a median of  $75 \text{ pg}/\text{m}^3$ . A multiple linear regression model incorporating temperature and time explained 32-43% of the variability in concentrations. The addition of an agricultural cycle to the model improved predictions by up to 7%. The model showed the agricultural cycle peaked in July, which corresponded with local endosulfan applications. Statistical analysis indicated that wind speed and wind direction did not significantly influence air concentrations in this study. Temperature and application season and frequency were mainly driving the air concentrations in the studied area. The atmospheric half-life of  $\alpha$ -endosulfan was estimated to be  $1.4 \pm 0.2$  years (Goel, et al., 2005).

To study regional transportation, the joint US EPA and Environment Canada monitoring project – Integrated Atmospheric Deposition Network (IADN) collected air samples in both US and Canada to investigate atmospheric loadings of toxic contaminants to the Great Lakes region. Seasonal measurements were conducted for  $\alpha$ - and  $\beta$ -endosulfan as well as endosulfan sulfate in vapor, precipitates, and adsorbed particle samples. The vapor phase results (1993-1998) showed a distinct annual cycle with peaks in summer one or two orders of magnitude higher than in winter. Summertime median values were around  $10 - 100 \text{ pg}/\text{m}^3$  with average of  $80 \text{ pg}/\text{m}^3$  and maximum  $> 700 \text{ pg}/\text{m}^3$  for  $\alpha$ -endosulfan. Concentrations for the  $\beta$ -isomer and endosulfan sulfate were generally lower. Annual average concentrations of  $\beta$ -endosulfan were  $15 \text{ pg}/\text{m}^3$  and  $5.5 \text{ pg}/\text{m}^3$  for the samples collected from Canadian and US stations, respectively. Median values between 10 and 100 were also determined for  $\beta$ -endosulfan at several sites in summertime. On average the concentrations measured for endosulfan sulfate were about  $5.5 \text{ pg}/\text{m}^3$  (US EPA, 2006b). In precipitation (1987-1997), the concentration of  $\beta$ -isomer was often higher than  $\alpha$ -isomer. For samples from lakes Superior and Erie, concentrations ranged  $0.13 - 1.95 \text{ ng}/\text{L}$  for  $\alpha$ -endosulfan, and  $0.19 - 6.09 \text{ ng}/\text{L}$  for  $\beta$ -endosulfan. Higher concentrations of  $0.54 - 8.22 \text{ ng}/\text{L}$  for

$\alpha$ - endosulfan and 1.06 – 12.13 ng/L for  $\beta$ -endosulfan were reported for the samples from Lake Michigan (Galarneau, et al., 2000). Average concentrations of endosulfan sulfate ranged 0.1 – 1 ng/L in precipitation samples from the Great Lakes region. IADN also measured endosulfan concentrations in airborne particulate (filter-retained) matter (1995-2000). Averaged concentrations were approximately 7.5 pg/m<sup>3</sup> for  $\alpha$ -endosulfan and 2.9 pg/m<sup>3</sup> for  $\beta$ -endosulfan. Seasonal differences for particles were much less pronounced as compared with the vapor phase data. Airborne dust endosulfan was measured on a cotton farm during the growing season in Australia. Total endosulfan ( $\alpha$ -,  $\beta$ -endosulfan and endosulfan sulfate) concentrations of the airborne dust were in a range of 0.07 to 1.04  $\mu$ g/g (Leys, et al., 1998).

Long-range atmospheric transportation was evidenced by widely distributed endosulfan in a pristine environment, the Arctic region, where endosulfan air concentrations ranged 4.2-4.7 pg/m<sup>3</sup> during 1993-1997 (Patton, et al., 1989; Halsall, et al., 1998; Hung, et al., 2002). In the eastern Arctic, endosulfan concentrations in air were reported between 1–10 pg/m<sup>3</sup> (De Wit, et al., 2002; Konoplev, et al., 2002).

Endosulfan air concentrations associated with pesticide application were monitored in both application and ambient studies in California. Pursuant to the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5), DPR provided endosulfan use report and air monitoring recommendations to Air Resource Board (ARB) for documenting the airborne endosulfan concentrations. ARB monitored an endosulfan application to an apple orchard in San Joaquin County in April 1997, and conducted ambient air monitoring during a period of high use of endosulfan in Fresno County in July-August 1996 (ARB, 1998). Both application and ambient air samples were collected by passing a measured volume of ambient air through XAD-2 resin tubes connected with a sampling pump at flow rate of 2.0 liters/minute. The samples were extracted using 3 ml of isooctane and analyzed on a gas chromatograph with a DB-608 capillary column and an electron capture detector. Both application and ambient samples were analyzed for  $\alpha$ -isomer,  $\beta$ -isomer and endosulfan sulfate concentrations.

For the application study, Thiodan 50 WP (50% w/w basis of active ingredient of endosulfan) was applied to a 6-acre field in an 8.5-acre orchard using ground-rig blower at 2.5 mph with small nozzle (#3 T-jet) at 200 pounds per square inch, and 200 mph fan. The application rate was 3 pounds of Thiodan 50 WP/acre (active ingredient of 1.5 pounds/acre) in 100 gallons of water. ARB collected four 12-hour background and twenty-eight application samples during seven sampling intervals at four sampling sites, one on each side of the application field. The sampling sites were approximately 7, 18, 9, and 11 yards from the edge of the treatment field, on the east, north, south, and west side, respectively. The air sampler at the east side was 2.5 feet above the field, while those at the other three sides were at the same elevation as the field. A meteorological station was positioned approximately 50 yards west of the northeast corner of the treatment field to determine wind speed and direction, relative humidity and air temperature. The duration of the seven sampling intervals were 3 (application plus 1 hour), 2, 4, 8, 9.5, 24, and 24 hours, respectively. The monitoring results are summarized in Table 11. The highest concentration for each of all sampling intervals was observed at the east side, downwind from the application area. The highest individual sample concentration was 4000 ng/m<sup>3</sup> (3800 ng/m<sup>3</sup>  $\alpha$ -isomer and 200 ng/m<sup>3</sup>  $\beta$ -isomer) in a 4-hour sample during the third sampling interval when the average wind speed was 1.35 mph. The second highest concentration, 1891 ng/m<sup>3</sup> (1800

ng/m<sup>3</sup>  $\alpha$ -isomer and 91 ng/m<sup>3</sup>  $\beta$ -isomer) was observed during the second sampling interval which had an average wind speed of 5.23 mph. The sum of  $\alpha$ -endosulfan and  $\beta$ -endosulfan for each sampling interval, and time-weighted-average (TWA) concentrations at each sampling site are presented in Table 12. The ratio of  $\alpha$ -isomer:  $\beta$ -isomer varied from 5 to 209 among all the samples with concentrations of both isomers above the limit of quantification (LOQ). Endosulfan sulfate was “detected” in 7 out of the 28 valid samples (“Detected” means concentration greater than or equal to limit of detection (LOD), but less than LOQ). None of the application samples were found above the LOQ of 19 ng/sample.

**Table 11. Summary of ARB’s application monitoring results (1997)**

Sampling Interval	Duration hours	Highest endosulfan concentration (ng/m <sup>3</sup> )*		
		$\alpha$ -isomer	$\beta$ -isomer	$\alpha$ - and $\beta$ -isomer
1	3	540	73	613
2	1.9	1800	91	1891
3	4	3800	200	4000
4	8.1	1200	73	1273
5	9.5	360	18	378
6	23.8	490	35	525
7	24	380	38	418
		$\alpha$ -isomer		$\beta$ - isomer
		Number	Percent	Number Percent
Total valid results**		28		28
Results were above LOQ		27	96%	16 57%
Results were “detected”		0	0%	2 7%
Results were below LOD		1	4%	10 36%

\*For the collocated samples, the average of the two sample results was used in this summary.

\*\*Laboratory reported LOD and LOQ in unit of ng/sample. ARB converted unit to ng/m<sup>3</sup> based on an 8-hour sampling air volume of 0.96 m<sup>3</sup>. In this summary, the unit conversion was based on actual air volumes sampled, 0.42, 0.23, 0.48, 0.97, 1.14, 2.85, and 2.88 m<sup>3</sup>, for each sequential sampling interval, respectively. The LOD and LOQ ranged 1 to 13 ng/m<sup>3</sup> and 3.5 to 43.5 ng/m<sup>3</sup> for  $\alpha$ -isomer, and 2 to 26 ng/m<sup>3</sup> and 6.6 to 82.6 ng/m<sup>3</sup> for  $\beta$ -isomer, respectively.



**Table 12. ARB's application monitoring results (ng/m<sup>3</sup>)\* during each interval at each site**

Interval	Hours	East	North	South	West
		7 yards (6.4 m)	18 yards (16.4 m)	9 yards (8.2 m)	11 yards (10 m)
1	3	613	605	513	338
2	1.9	1891	474	493	56
3	4	4000	751	1252	27
4	8.1	1273	461	133	13
5	9.5	378	99	69	4
6	23.8	525	88	445	19
7	24	418	57	338	5

Cumulated Hours		Time Weighted Average			
	3	613	605	513	338
	5	1109	554	505	229
	9	2408	643	841	138
	17	1867	556	504	79
	27	1333	392	348	52
	50	951	248	394	36
	74	779	187	376	26

\*Results were sum of  $\alpha$ -endosulfan and  $\beta$ -endosulfan. If a collocated sample was collected, the average of the collocated sample results was used for calculation. If a sample was reported as <LOD, the quantity of half the LOD was used for concentration calculations. If sample was reported as “detected”, the quantity of half the (LOD + LOQ) was used for concentration calculations.

For ambient monitoring, ARB collected 24-hour samples four days a week for five weeks at four monitoring locations. The selected monitoring locations were populated areas, such as schools, and surrounded on all directions by farmland. On the surrounding farmland, cotton was planted approximately 50 to 100 yards from two monitoring locations and  $\frac{3}{4}$  to 2 miles from the other two locations. Samplers were positioned about 1.5 meters above the rooftops of single-story buildings. In addition, a background location was selected in downtown Fresno and the sampler was positioned on top of a two-story building. A total of 75 monitoring sample results were reported which excluded 20 background samples and 5 invalid samples. The highest 1-day and the second highest 1-day individual results were 166 and 138 ng/m<sup>3</sup> endosulfan, respectively. The highest weekly TWA and highest 5-week TWA were 88 and 30 ng/m<sup>3</sup> endosulfan, respectively (Table 13). All the highest concentrations occurred at one site in the town of San Joaquin. This site was three quarters to one mile from the closest crop fields in different directions (Table 14). All background results were below the LOD except for two “detected” for  $\alpha$ -isomer, but not quantifiable. There was no endosulfan sulfate found in any of the ambient samples with LOQ of 37 ng/sample. Endosulfan use queried from DPR's PUR database showed that within the townships/ranges where the ARB's monitoring sites were located, endosulfan use during the monitoring period varied from 0 to 1,288 pounds of active ingredients. The data indicated that the higher air concentrations were related to higher local use during the monitoring period. However, in Fresno County the highest endosulfan monthly use, 24,498 pounds, was in July, followed with 20,797 pounds in June and 14,158 pounds in August 1996. A total of 19,785 pounds endosulfan was used during ARB's ambient monitoring period (July 29, 1996 to August

29, 1996). This monitoring was slightly off the peak use month in July. DPR recommended the ambient monitoring to be conducted in July and August, 1996 (DPR, 1996).

**Table 13. Summary of ARB’s ambient monitoring results (1996)**

	Endosulfan concentration (ng/m <sup>3</sup> )		
	$\alpha$ -isomer	$\beta$ -isomer	$\alpha$ - + $\beta$ -isomers
Limit of detection (LOD)*	1.2	3.8	
Limit of quantification (LOQ)*	3.8	12	
Highest 1-day air concentration	140	26	166
2 <sup>nd</sup> highest 1-day air concentration	125	13	138
Highest weekly average			88
Highest 5-week average			30

	$\alpha$ -isomer		$\beta$ - isomer	
	Number	Percent	Number	Percent
Total valid results**	75		75	
Results were above LOQ	66	88%	2	3%
Results were “detected”	9	12%	29	39%
Results were below LOD	0	0%	44	59%

\*based on a 24-hour sampling period at 2 L/minute.

\*\*Urban background samples were not included.

**Table 14. ARB's ambient monitoring results (ng/m<sup>3</sup>)\* at each site**

<b>Sampling Date</b>	<b>Cantua Creek</b>	<b>San Joaquin</b>	<b>Tranquility</b>	<b>Five Points</b>
<b>Distance to fields</b>	<b>50-100 yard</b>	<b>0.75-1 miles</b>	<b>1-2 miles</b>	<b>50-100 yard</b>
7/29/1996	10.2	24.9	28.9	10.4
7/30/1996	36.9	23.9	27.9	30.9
7/31/1996	42.4	19.9	22.4	19.9
8/1/1996	11.9	23.9	8.8	15.9
8/5/1996	34.9	6.3	48.9	Invalid
8/6/1996	31.9	42.9	77.9	16.9
8/7/1996	30.9	138	41.9	15.9
8/8/1996	24.9	166	42.9	24.9
8/12/1996	25.9	20.9	10	9.9
8/13/1996	27.9	26.9	24.9	11.9
8/14/1996	21.9	11.3	11.25	7.6
8/15/1996	10.9	12.9	52.9	6.1
8/19/1996	11	4.4	7.8	6.3
8/20/1996	10.9	10.7	13.9	7.8
8/21/1996	8.45	11.95	24.4	7
8/22/1996	Invalid	Invalid	Invalid	Invalid
8/26/1996	4.4	4.4	4.4	4.4
8/27/1996	4.4	4.4	7.5	4.4
8/28/1996	6.45	6.15	7.8	4.4
8/29/1996	6.6	11.9	20.9	7
Township/Range	16S/15E	15S/16E	15S/16E	17S/17E
Endosulfan use (pounds)	953	1,288		0

\*Results were sum of  $\alpha$ -endosulfan and  $\beta$ -endosulfan. In case that collocated samples were collected, average of the collocated sample results was used for calculation. If a sample was reported as <LOD, the quantity of half the LOD was used for concentration calculations. If sample was reported as "detected" the quantity of half the (LOD + LOQ) was used for concentration calculations.

In an earlier study, CDFA monitored ambient air for multiple pesticides in a residential area near Salinas, Monterey County, in June 1985, a historically high pesticide use month in the Salinas Valley (Sava, 1985). Consecutive 6-hour air samples were collected for three days from June 18 to June 21 at each of three sampling sites. The three sites were located at the west, north, and south side of the city of Salinas and 1200, 190, and 50 feet from agricultural fields, respectively. Monterey County Agricultural Commissioner's staff had previously collected leaf samples and documented the presence of endosulfan. Air samples were collected using low volume air samplers at flow rate of 32 L/min. In 6 of total 36 samples (17%),  $\alpha$ -endosulfan was found above the method detection limit (MDL) of 9 ng/m<sup>3</sup>. Five detections occurred in the morning time (Table 15) coinciding with the time of high agricultural activities and low wind speed, and one was found during nighttime when pesticide application activity was low and wind speed was relatively high. The wind direction was consistently out of the northwest during the monitoring study.

**Table 15. Quantifiable  $\alpha$ -endosulfan results during DPR ambient monitoring in 1985**

Date	Time	$\alpha$ -endosulfan (ng/m <sup>3</sup> )	Wind speed* (mph)	Wind direction*
6/19/1985	18:00-24:00	51	6	315°
6/20/1985	24:00-6:00	42	4	315°
6/20/1985	6:00-12:00	34	4	210°
6/21/1985	6:00-12:00	34	5	330°
6/21/1985	24:00-6:00	35	2	290°
6/21/1985	6:00-12:00	36	5	330°

\*Recorded by meteorological station located near location in the western section of the city.

US EPA concluded in their RED that while atmospheric transport has been documented for endosulfan, the available data is not sufficient to evaluate its potential impacts on non-target organisms. The limited data available show measured concentrations significantly lower than those used in the Agency's risk assessment but exposures to more sensitive species are possible (US EPA, 2002)

### **Fate and persistence in water/sediments**

#### ***Spray drift and runoff transportation***

Endosulfan contamination of surface water bodies is due mainly to spray drift and runoff transportation. Spray drift consists of both  $\alpha$ - and  $\beta$ -isomers from pesticide application and is deposited on off-target water body and other surfaces. Runoff events result in soil erosion and horizontal transport of endosulfan a short or long distance. This transportation route can carry all three types of endosulfan ( $\alpha$ -isomer,  $\beta$ -isomer, and endosulfan sulfate) and most likely be dominated by endosulfan sulfate due to its persistence for long enough time to be transported. In a study of nine storm event samplings, endosulfan was detected in four different waterways. The highest concentrations, >1  $\mu\text{g/L}$ , were observed with endosulfan sulfate making up 50%-70% of the total endosulfan. There were a few periods when the sum of  $\alpha$ - and  $\beta$ -isomers was dominated, but with short duration.  $\alpha$ - and  $\beta$ -isomers remained in the river for only a few days, whereas endosulfan sulfate remained for months (Briggs, et al. 1998).

In California, movement of endosulfan into surface water via rainfall runoff and irrigation drainage was evidenced in the Moss Landing Drainage area of Monterey County, where increasing endosulfan residues were detected in mollusk, an indicator organism of chemical contamination. Sediment and water samples were collected with minimum sample sizes of 22 and 11, respectively, at each of three locations. With detection limit of 1.0 ppb,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate residues were detected in 33%, 33%, and 25% of sediment samples, respectively. With detection limit of 0.02 ppb, 25% of the water samples contained detectable endosulfan sulfate. These results showed that endosulfan moved off-site into this drainage area (Gonzalez, et al. 1987). A further monitoring study in three treated fields was

conducted in this area in 1988. Results of rain runoff samples showed that endosulfan residues were detected in all three fields at concentrations ranging 2.2 to 13 mg/L (Fleck et al., 1991).

#### ***Adsorption/desorption and volatilization***

One main process for endosulfan loss from water is adsorption/desorption. Once entering into the surface water bodies, endosulfan can be rapidly removed via adsorption onto suspended matter towards a dynamic equilibrium with aqueous endosulfan concentration. However, the real equilibrium may not be reached for an extended time due to kinetic energy barrier in natural environment. Sedimentation moves particle-bounded endosulfan to sediment. In the River Rhine in Europe more than 75% of the endosulfan was found to be associated with particulate matter (Greve and Wit, 1971). Adsorption/desorption can be reversible or irreversible depending on adsorption mechanisms. In general, adsorption by electrostatic force is reversible, while by ligand exchange at a specific site is irreversible. Even for a reversible process, a laboratory batch experiment showed that  $\alpha$ -endosulfan was more readily desorbed from sediments than  $\beta$ -endosulfan (Peterson and Batley, 1993).

Another abiotic route for endosulfan loss from water is volatilization to atmosphere. Volatilization is driven by Henry's Law constant and affected by weather conditions. In a laboratory study, 24 hours evaporation at room temperature resulted in 26-27%  $\alpha$ -endosulfan loss, but 95-98%  $\beta$ -endosulfan remained in the incubation vials (Peterson and Batley, 1993).

#### ***Degradation and overall dissipation***

Two main processes of aqueous endosulfan degradation are hydrolysis and oxidation. Hydrolysis favors in neutral to alkaline water ( $\text{pH} \geq 7$ ). A main degradation product is endosulfan diol which is less toxic and can be further degraded (Figure 8). Hydrolysis rates vary for both  $\alpha$ - and  $\beta$ -endosulfan depending on pH and temperature (Table 16). In a laboratory study at 20°C and pH 7.2-9.4, the log of the hydrolysis rate constants were linear to pH with similar slopes for both of  $\alpha$ - and  $\beta$ -endosulfan (Peterson and Batley, 1993). Hydrolysis of endosulfan sulfate is slower than either of parent isomers and was found insignificant in river water (Briggs, et al. 1998). Endosulfan hydrolysis can be both abiotic and biotic processes. Miles and Moy (1979) reported that microbial hydrolysis degraded  $\alpha$ -endosulfan faster than  $\beta$ -endosulfan and Peterson and Batley (1993) reported chemical hydrolysis degraded  $\beta$ -endosulfan faster than  $\alpha$ -endosulfan.

**Table 16. Summary of hydrolysis half-lives (days) at different temperature and pH**

Temperature (°C)	pH	Autoclaved		Non-autoclaved	
		$\alpha$ -endosulfan	$\beta$ - endosulfan	$\alpha$ -endosulfan	$\beta$ - endosulfan
Reported by EPA (2001)*					
25	5	14.7	91.2	103.5	13.3
25	5	>200	>200		
25	7	11	19		
25	9	4	6		
Study by Hengpraprom and Lee, 1998 **					
30	5	17.2	277.3	18.8	22.5
40	5	99.0	67.3	55.9	23.9
25	8	3.3	3.1	2.6	2.5
30	8	1.5	1.4	2.2	1.5
40	8	1.3	0.9	1.1	0.8
Study by Peterson and Batley, 1993***					
20 (HRW)	7.2			48.9	22.2
20 (SRW)	7.4			41.3	14.4
20 (SRW)	7.7			20.6	7.6
20 (SRW)	8.1			5.8	3.2
20 (HAW)	8.4			2.4	1.4
20 (SRW)	8.5			4.4	1.9
20 (SRW)	8.4	3.1	1.4		
20 (HAW)	8.9	1.3	0.5		
20 (HRW)	9.0			1.3/2.2	0.6/1.2
20 (SRW)	9.4	0.5	0.4		
4 (HAW)	8.5	NA****	10.3		

\*batch method with sterilized aqueous pH buffer solutions, incubated for 30 days

\*\*batch method with distilled/deionized water suspension, pH adjusted with 0.1 M HCl and 0.1 M Na<sub>2</sub>HPO<sub>4</sub>·12 H<sub>2</sub>O, incubated for 8 days

\*\*\*HRW, SRW, and HAW refer to hard river water, soft river water, and hard artificial water, respectively. Half-lives were calculated from rate constants reported in this study.

\*\*\*\*not able to calculate since hydrolysis of  $\alpha$ -endosulfan was not detectable over 8 days.

Under anaerobic conditions, endosulfan hydrolysis was slower. In laboratory study under “oxygen-limited conditions” with incubated 10 ppm endosulfan (50 ppm endosulfan sulfate due to its higher analytical detection limit) in sterilized water or soil water extracts, half-lives were 97 days, >200 days, and >> 200 days for  $\beta$ -endosulfan,  $\alpha$ -endosulfan, and endosulfan sulfate, respectively. These half-lives were estimated using 0-30 days data with the first order exponential decay model. Half-life of endosulfan sulfate in the sterile water was 30 days in unsealed vessels versus 103 days in sealed vessels (Guerin, 2001).

In acidic water (pH < 7), microbial oxidation of  $\alpha$ - and  $\beta$ -endosulfan to endosulfan sulfate is a major degradation path. Majority of surface water bodies have pH values around 7. Both hydrolysis and oxidation can occur. However, there are ecologically important acidic creeks,

small rivers and lakes with low buffer capacity (Henriksen, et al., 1997) where endosulfan contamination may be of concern due to its persistence. In alkaline seawater, endosulfan hydrolysis to diol is deemed to be the main degradation process.

The overall degradation half lives in natural water bodies with suspended matter and sediments, are affected by macro and micro-scale conditions, such as redox potential and pH in pore water of soils and sediments, microbial organism population, organic matter content, and so on. Most aquatic sediments have a shallow aerobic top layer and prevalently anaerobic conditions in deeper layers. US EPA (2001) reported that in aerobic conditions, 50% of the total  $\alpha$ - and  $\beta$ -endosulfan dissipated within approximately 2 weeks, and approximately 3 weeks for endosulfan sulfate in neutral to alkaline water and sediments. They are more persistent in acidic to neutral system.

In a modular estuarine mesocosm study (Walse, et al., 2003), the overall half lives of  $\alpha$ -,  $\beta$ -, and technical grade endosulfan were estimated to be 29.3, 25.1, and 27.6 hours, respectively. At 100 hours, mass balances of 56.5%, 80.7% and 71.1% were obtained for  $\alpha$ -,  $\beta$ -, and technical grade endosulfan, respectively. The low mass balance of  $\alpha$ - endosulfan might be due to volatilization loss which was not quantified in this study. Endosulfan sulfate formation in the mesocosm treated with  $\beta$ -endosulfan was 65% less than with  $\alpha$ -endosulfan. This was explained due to preferential metabolic oxidation of  $\alpha$ -endosulfan over  $\beta$ -endosulfan.

In aerobic river water/sediment systems with water pH of 7.3 and gravel pit pH of 7.8, endosulfan had a short residence time in the water phase and was readily transferred to bottom sediment. Half-lives of 12 and 10 days were estimated for the parent endosulfan in the system, whereas 21 days and 18 days were estimated for endosulfan plus endosulfan sulfate and endosulfan carboxylic acid (Stumpf, 1990). Similar results were obtained from another freshwater/sediment study that included two types of sediment, a sandy sediment with a carbon content of 0.1% and a clay loam sediment with 3.2% organic carbon (Jonas, 2002). Half-lives in water phase were 0.7 days in the clay loam and 1.6 days in the sand sediment system. The half-lives for the entire water/sediment system were 3.6 days for the clay loam and 35.1 days for the sand. In the loamy system, the initial supernatant water had a pH of 7.8 and kept in a narrow range around pH 8, but in the sandy system the initial water pH of 7.9 declined to approximately 7. The biomass was 61.6 versus 2.3 mg carbon/100g in the two systems. Endosulfan metabolites, endosulfan sulfate and endosulfan-diol, endosulfan hydroxyl carboxylic acid were formed in both systems. Release of  $^{14}\text{CO}_2$  from the isotope labeled chlorinated moiety of the molecule was insignificant with 0.7% and 1.1% from the two systems, respectively, over 120 days of the study period.

In a seawater study, filtered but unsterilized seawater (pH 8.0) in half-liter flasks incubated under laboratory light at 20 °C for 40 days, half-lives were 4.9 days and 2.2 days for  $\alpha$ -endosulfan and  $\beta$ -endosulfan, respectively. In a seawater/sediment microcosm study, unsterilized 7-cm sediment cores taken from a tidal creek at low tide with 130 ml of overlying seawater (pH 7.3-7.7) incubated under laboratory light at 20 °C for 20 days, half-lives of 22 days and 8.3 days was determined for  $\alpha$ -isomer and  $\beta$ -isomer, respectively. Endosulfan diol was identified as a

degradation product (Cotham and Bidleman, 1989). The longer half-lives in seawater/sediment system than those in seawater indicated an endosulfan adsorption onto sediments to compete with degradation.

### ***Water concentrations in California***

#### **Surface water**

California surface water monitoring data was queried from DPR's surface water monitoring inventory database (DPR, 2007c). The water samples were collected statewide by multiple state and local agencies and other organizations. From 1990 to the end of May 2007, a total of 816 samples for  $\alpha$ -endosulfan, 816 samples for  $\beta$ -endosulfan, and 1387 samples for endosulfan sulfate were analyzed. Samples were mainly collected in the years from 1991 to 1995 for all three endosulfan forms, and from 2001 to 2004 for endosulfan sulfate only. Endosulfan was found in less than 10% of samples.  $\alpha$ -endosulfan in 41 (5.0%),  $\beta$ -endosulfan in 41 (5.0%), and endosulfan sulfate in 127 (9.2%) samples were above the method detection limits (MDLs). The MDLs ranged from 0.00005 to 0.1  $\mu\text{g/L}$  for all three analytes. The lowest concentration detected for all three analytes was 0.005  $\mu\text{g/L}$ ; and the highest concentrations were 0.220, 0.039, and 0.628  $\mu\text{g/L}$  for  $\alpha$ -,  $\beta$ -endosulfan, and endosulfan sulfate, respectively (Table 17). The detections for  $\alpha$ - and  $\beta$ -endosulfan occurred in three counties, Imperial, Sacramento, and Stanislaus, while endosulfan sulfate was detected in four more counties, Los Angeles, Merced, San Joaquin, and Ventura (Table 18). However, except for Imperial County, none of them were listed in Table 4, which listed the counties with mean annual endosulfan use that exceeded 1,000 pounds for the years 1996 to 2005. Although there were no data for the Colorado River itself, endosulfan detections in the Colorado River Basin were reported in the early 1990s. All 36 detections were in the Alamo River in Imperial county and concentration ranged from 0.008 to 0.22  $\mu\text{g/L}$ .

In addition, along a transect from the Central Valley to Sequoia National Park, water samples collected from eight sites in 1997 contained  $\alpha$ -endosulfan and  $\beta$ -endosulfan ranging from 0.9 – 24.8 ng/L and 0.41 – 140.5 ng/L, respectively (LeNoir *et al.*, 1999). Water samples collected from two lakes in the Sierra Nevada Mountains in 1997 contained endosulfan with concentrations from 0.3 to 1.0 ng/L of  $\alpha$ -endosulfan, from 0.17 to 1.8 ng/L of  $\beta$ -endosulfan, and from 0.33 to 2.9 ng/L of endosulfan sulfate (Fellers *et al.*, 2004). Endosulfan was also detected in Lake Tahoe and concentrations ranged from <0.004 to 0.26 ng/L at different depths (McConnell, et al., 1998).

Endosulfan residues were also detected in sediment (Gonzalez *et al.*, 1987; Fleck *et al.*, 1991; Ganapathy *et al.*, 1997; Weston *et al.*, 2004) and aquatic organisms, such as mussels (Singhasemanon, 1996), amphibians (Sparling *et al.*, 2001), fish (Singhasemanon, 1995; Brodberg and Pollock, 1999), and frog tissues (Fellers, et al., 2004) and concentrations varied.



**Table 17. Summary of surface water monitoring results for endosulfan in each year\***

Year	$\alpha$ -Endosulfan			$\beta$ - Endosulfan			Endosulfan sulfate		
	Samples number	Detects Number	Concentrations $\mu\text{g/L}$	Samples number	Detects number	Concentrations $\mu\text{g/L}$	Samples number	Detects number	Concentrations $\mu\text{g/L}$
1990	0	0	NA	0	0	NA	9	0	NA
1991	220	2	0.012 to 0.022	220	3	0.005 to 0.045	273	43	0.005 to 0.20
1992	229	2	0.005 to 0.008	229	2	0.006 to 0.008	213	18	0.010 to 0.10
1993	125	31	0.008 to 0.220	125	32	0.005 to 0.170	125	48	0.020 to 0.580
1994	134	5	0.016 to 0.068	134	4	0.024 to 0.039	134	5	0.023 to 0.628
1995	105	0	NA	105	0	NA	108	0	NA
1996	3	1	0.002	3	0	NA	3	1	0.12
2001	0	0	NA	0	0	NA	15	6	0.002 to 0.005
2002	0	0	NA	0	0	NA	221	0	NA
2003	0	0	NA	0	0	NA	258	5	0.002 to 0.005
2004	0	0	NA	0	0	NA	28	1	0.002
<b>Total</b>	<b>816</b>	<b>41</b>		<b>816</b>	<b>41</b>		<b>1387</b>	<b>127</b>	

\*Data was queried from California Department of Pesticide Regulation Surface Water Database (DPR 2007c).

**Table 18. Summary of surface water monitoring results for endosulfan in each county with positive detections\***

County	Samples analyzed			Endosulfan Detections						Highest Concentrations		
	$\alpha$ -	$\beta$ - number	sulfate-	$\alpha$ -	$\beta$ - number	sulfate-	$\alpha$ -	$\beta$ - %	sulfate-	$\alpha$ -	$\beta$ - $\mu\text{g/L}$	sulfate-
Imperial	65	65	132	36	36	59	55	55	45	0.22	0.17	0.58
Los Angeles			127			9			7			0.022
Merced			190			1			0.5			0.12
Sacramento	188	188	62	1		2	0.5		3	0.002		0.05
San Joaquin			17			2			12			0.2
Stanislaus	238	238	285	4	5	50	1.7	2.1	18	0.22	0.045	0.18
Ventura			7			4			57			0.005
<b>Total</b>				<b>41</b>	<b>41</b>	<b>127</b>						

\*Data was queried from California Department of Pesticide Regulation Surface Water Database (DPR 2007c).

### Ground water

The Pesticide Contamination Prevention Act requires DPR to maintain a statewide database of wells sampled for pesticide, and state and local agencies to submit results of well sampling for active ingredients to DPR (Nordmark, et al., 2006). Troiano et al. (2001) described the well water monitoring program in details, including criteria for selection of wells, sampling methods, and analytical methods.

Well monitoring data is summarized in Table 19. The samples were collected and analyzed by multiple agencies and organizations including DPR (Nordmark, et al., 2006). From 1984 to 2005, total of 4,320, 111, and 3,647 well water samples were analyzed and detected in 12, 0, and 3 samples for  $\alpha$ -endosulfan,  $\beta$ -endosulfan, and endosulfan sulfate, respectively. Concentrations ranged from 0.01 – 34.7  $\mu\text{g/L}$  for  $\alpha$ -endosulfan and 0.15-0.48  $\mu\text{g/L}$  for endosulfan sulfate with detection limits ranging 0.01-0.05  $\mu\text{g/L}$  for  $\alpha$ -endosulfan and 0.1-0.2  $\mu\text{g/L}$  for endosulfan sulfate. However, all 15 detections were classified as “unverified,” because they were not detected in follow-up samples. None detection was ever for  $\beta$ -endosulfan.

**Table 19. Summary of endosulfan well water monitoring results (1984-2005)\***

Year	Samples number	$\alpha$ - Endosulfan		Endosulfan Sulfate		
		Detections number	concentration ppb	samples number	detections number	Concentration ppb
1984	339	3	0.02-4.5	219		
1985	661	1	0.2	565		
1986	401	1	0.01	218		
1987	421			256		
1988	198			114		
1989	86			89		
1990	44			44		
1991	13			13		
1992	34	5	0.05-34.7	35	2	0.22-0.48
1993	66			60		
1994	187	2	0.45	186		
1995	203			201	1	0.15
1996	19			18		
1997	0			0		
1998	10			10		
1999	22			24		
2000	24			24		
2001	5			4		
2002	143			147		
2003	957			956		
2004	117			117		
2005	296			294		
NS**	74			53		
<b>Total</b>	<b>4320</b>	<b>12</b>		<b>3647</b>	<b>3</b>	

\*Data was queried from the DPR's Well Inventory Database (DPR, 2007d)

\*\*Year was not specified in the database.

### **Regional and remote transportation**

Endosulfan can travel long distances and has been detected all over the world, even in the Arctic. Long range or medium range regional transportation usually involves multiple processes and routes occurring simultaneously in determining ultimate environment fate of endosulfan. Volatilization, vapor transportation, and runoff transportation are the main routes for endosulfan long range and regional transportations.

Pesticide contaminations related to regional transportation from Central Valley, California to the Sierra Nevada mountain range were investigated from 1995 to 1997. Table 20 summarized results of three studies related to this investigation. In summertime, LeNoir, et al. (1999) collected samples of air and dry particulate deposition from three locations at elevation of 200, 533, and 1,920 meters, respectively. Duplicated 1-day surface water transect samples were collected from the Central Valley through Sequoia National Park at six elevations from 118 to 2,042 meters. Additional surface water samples were collected from an elevation of 3,231 meters in the Kings Canyon National Park, and 3,322 meters within the Sequoia National Park. In wintertime, McConnell, et al. (1998) collected samples of precipitation, rain and snow, from three locations at elevations of 533, 1,920, and 2,200 meters, respectively. Lake Tahoe water samples were collected from the surface to a depth of 150 meters at the north site, and to a depth of 350 meters at the south sites. In addition, Fellers, et al., 2004, collected water and tissue samples of yellow-legged frog at two locations. Among all samples collected in the three studies, the highest endosulfan concentration (sum of  $\alpha$ -,  $\beta$ -, and sulfate endosulfan, if any) was 3.9 ng/m<sup>3</sup> for air, 3.6 ng/m<sup>2</sup>/day for dry particulate deposit, 165.3 ng/L for water, 7.9 ng/L for rain, 3.5 ng/L for snow, and 1.4 ng/g for frog tissue on a wet weight basis. Endosulfan, predominantly  $\alpha$ -endosulfan was found in all air samples and three of the seven dry particulate deposition samples had detectable concentrations of endosulfan. These samples were collected in May to September, 1996, which corresponded with the peak endosulfan use months in the Central Valley, California (Table 5). Three out of the top five endosulfan use counties (Table 4), Fresno, Kings, and Tulare, are in the Central Valley.

The Central Valley is an intensive agricultural area lying upwind of the west foot of the Sierra Nevada mountain range. During summer months, delta breezes and prevailing winds can transport endosulfan eastward to the mountain range and deposit as dry particulate on water bodies and ground surfaces. Even at elevations higher than 1,900 meters, endosulfan has been detected in air, particulate, and water samples. In wintertime, endosulfan use was minimum (Table 5) even in the top six use counties (Figure 5), but spraying of dormant orchards in the Central Valley may result in endosulfan in the air, fog, and rain droplet which can be, in turn, be transported to and precipitate, as wintertime rain and snow, in the Sierra Nevada mountain range. In addition, endosulfan transported in summertime may redistribute within the ecosystem of the Sierra Nevada mountain range based on its moderate volatility, adsorption and persistence properties. Endosulfan concentrations in the Lake Tahoe basin water (Fellers, et al., 2004) and snow (McConnell, et al., 1998) samples were generally lower than those from Sequoia National Park which may be explained by the shorter distance from the Central Valley to the Sequoia National Park (McConnell, et al., 1998).

**Table 20. Summary of monitoring results from three studies in Sierra Nevada Mountains**

Type	Samples		Detections		Unit	The highest concentrations			
	Location #	Number #	#	%		Endosulfan			Total*
						$\alpha$ -	$\beta$ -	sulfate	
Summertime sampling in 1996-1997 (LeNoir, et al. 1999)									
Air	3	12	12	100	ng/m <sup>3</sup>	3.7	0.6	0.07	3.9
Particulate	3	7	3	43	ng/m <sup>2</sup> /day	0.7	3.6	**	3.6
Surface water	8	8 x2***	8	100	ng/L	24.8	140.5	**	165.3
Wintertime sampling in 1995 – 1996 (McConnell, et al., 1998)									
Rain	1	7	**		ng/L	6.5	1.4	**	7.9
Snow	2	8	**		ng/L	3.0	0.5	**	3.5
Tahoe water	2 x4 depths	8	**		ng/L	0.3		**	0.3
Amphibian tissue sampling in 1997 (Fellers, et al., 2004)									
Surface water	2	4	4	100	ng/L	1.0	1.8	2.9	4.1
Frog tissue	2	40	32	80	ng/g wet wt	1.4	**	**	1.4

\*Sum of the reported  $\alpha$ -,  $\beta$ -, and sulfate endosulfan for an individual sample.

\*\*No specified data available.

\*\*\*Duplicate samples were collected at each of 8 locations and the average of the two was reported for each location

A similar investigation was conducted in 1986-1988 to look at spray drift and rain runoff from an endosulfan application to a state ecological reserve area, Moss Landing Drainage in Monterey County, California. Following an endosulfan application, CDFA staff collected water, runoff, soil, and sediment samples at the Moss Landing drainage area and in agricultural areas of the Salinas and Carmel River Valleys to evaluate endosulfan distribution (Gonzalez, et al. 1987; Fleck, et al., 1988). For samples collected from Moss Landing Drainage in 1996, endosulfan was detected in 58% of soil and 52% of sediment samples. On a dry weight basis, the highest concentrations of  $\alpha$ -,  $\beta$ -, and sulfate endosulfan were 310, 960, 160  $\mu\text{g/kg}$  in soil, respectively, and 52, 1300, and 160  $\mu\text{g/kg}$  in sediment, respectively. The results of the samples from the agricultural area did not support an even distribution for endosulfan. Only 8%, 9%, and 27% of the samples had detectable concentrations of  $\alpha$ -,  $\beta$ -, and sulfate endosulfan, respectively (Fleck, et al., 1988). Sediment samples collected from Moss Landing Drainage indicated also an uneven distribution of endosulfan (Gonzalez, et al. 1987). In a spray drift and rain runoff study (Fleck, et al., 1991), deposition, soil, and water samples were collected. An average between 0.005 and 0.019 kg/ha was reported on deposition samples 5.5 meters from the borders of the application field. In addition, rain runoff samples ranged from 2.2 to 13  $\mu\text{g/L}$  indicating another route of off-site movement of the applied endosulfan. The average of soil endosulfan was 1,548 and 2,962  $\mu\text{g/kg}$  for pre- and post-application. These results were comparable with other study in this region.

In Europe, atmospheric deposition of endosulfan on mountain lakes in the Alps, Pyrenees, and Caledonian Mountains was estimated between 0.2 – 340  $\text{ng/m}^2\text{-month}$  (Carrera, 2002). The southern lakes contained higher concentrations, reflecting the agricultural activities in southern Europe. In the northern lake only the more recalcitrant endosulfan sulfate was detected.

Studies have shown that endosulfan has even been transported to the Arctic. It has been detected in both east (Russia) and west (Canada) sides in atmospheric air, rain, snow, ice and fine particulate, water ways of lake, river, and sea, sediment, soil, plants, and amphibians, etc (Gregor and Gumme, 1989; Barrie, et al., 1992; Blais, et al., 1998; Konoplev, et al., 2002; De Wit, et al., 2002; Chernyak, et al., 1996). Mean water concentrations ranged from 2-10  $\text{pg/L}$  (INAC, 2002). Seasonal trends showed increasing concentrations during the open water season suggesting fresh input from gas exchange and runoff. This trend parallels seasonal trends observed in Arctic air. The spatial distribution of organochlorine pesticides spanned the Arctic Ocean from the Bering and Chukchi seas to the North Pole, to a station north of Spitsbergen, and then south into the Greenland Sea. Spatial differences in concentration varied with the observed pesticide. A reverse trend was found for endosulfan, with lower concentrations in the ice-covered regions (Jantunen and Bidleman, 1998).

Briggs, et al. (1998) monitored endosulfan concentrations in rivers and daily rainfall observations from 23 stations in a cotton production region for five years. On plotting  $\alpha$ - and  $\beta$ -endosulfan fractions of each observed peak concentration versus antecedent rainfall events, it was found that endosulfan concentration peaks fell mainly into two distinct regions: (a) events with little antecedent rainfall and high fractions of  $\alpha$ - and  $\beta$ -endosulfan primarily by airborne transport, and (b) events with high antecedent rainfall and low fractions of  $\alpha$ - and  $\beta$ -endosulfan primarily by waterborne transport. Some events occurred in a third region (c) with low antecedent rainfall and low fractions of  $\alpha$ - and  $\beta$ -endosulfan, but arising from the continued

presence of endosulfan sulfate with a long riverine residence time. Very few events are observed in the fourth region with high antecedent rainfall and high fractions of  $\alpha$ - and  $\beta$ - endosulfan. Events in regions (a) and (b) were both of significant magnitude, with (a) being dominant at locations close to cotton farms. The data analysis indicated that airborne transport accounted for a significant fraction, around 50%, of the endosulfan concentrations in slow-flowing waterways close to cotton farms. Waterborne transport could only occur after rainfall. Dust transport and subsurface leaching were of negligible magnitude for endosulfan regional transport.

### **Fate and persistence in biota**

Endosulfan is not persistent in biota and not susceptible to bioaccumulation. Therefore, it is not hazardous if applied at recommended rates and following the label instructions. For terrestrial animals and most aquatic organisms, it is metabolized very fast to a low plateau level of residues. On the other hand, endosulfan is highly toxic to some aquatic species, particularly fish. Fish are extremely sensitive to endosulfan. Fish kills due to discharge of endosulfan into rivers have been reported. Application of endosulfan to wetlands at recommended rates may well result in killing of fish. Half lives of  $\alpha$ -,  $\beta$ -, and  $\alpha$ - +  $\beta$ -endosulfan were estimated of  $2.01 \pm 0.44$ ,  $1.74 \pm 0.33$ ,  $1.81 \pm 0.35$  days, respectively for the fish species Yellow Tetra (*Hyphessobrycon bifasciatus*) (Jonsson and Toledo, 1993). An anti-oxidant, selenium, was claimed to reverse the toxic implication of endosulfan in fish (Shafiq-ur-Rehman, 2006). Endosulfan is moderately toxic for honey bees. Toxicity for birds is high in a laboratory setting, but no poisonings have been reported under field conditions.

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